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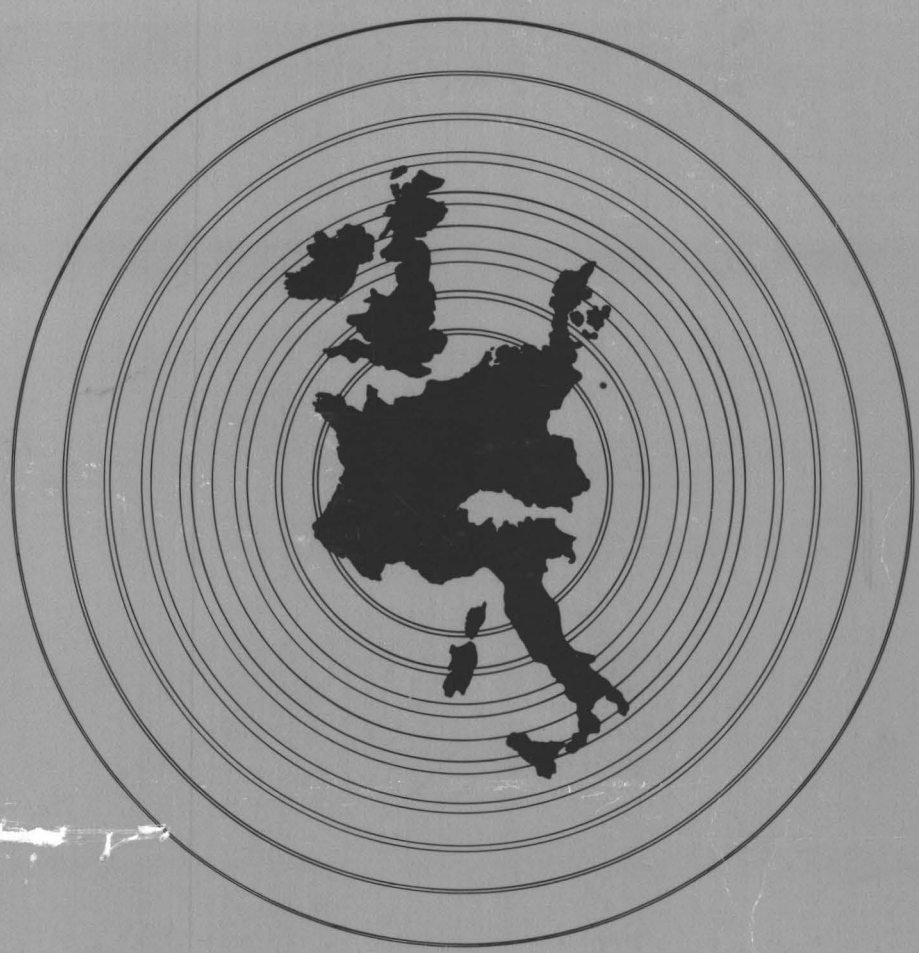

FIRST PETTEN COLLOQUIUM ON ADVANCED HIGH TEMPERATURE MATERIALS:

TECHNOLOGICAL AND INDUSTRIAL ASPECTS

January 29 and 30, 1976
Petten, the Netherlands

Editions MASSON
120, Bd. Saint-Germain
F-75280-Paris-06
FRANCE

FIRST PETTEN COLLOQUIUM

ON

ADVANCED HIGH TEMPERATURE MATERIALS: TECHNOLOGICAL AND INDUSTRIAL ASPECTS

PETTEN (THE NETHERLANDS), JANUARY 29-30, 1976

Organized by

THE COMMISSION OF THE EUROPEAN COMMUNITIES, Joint Research Center, Petten

FIRST PETTEN COLLOQUIUM
ON
ADVANCED HIGH TEMPERATURE MATERIALS:
TECHNOLOGICAL AND INDUSTRIAL ASPECTS

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PREFACE

Ever since industrial activities have been making use of high-temperature technology, the increase of operating temperatures has been a vital endeavour, which finds its most serious obstacles in the natural limits of available materials.

Being aware of the still growing need for industrial application of high temperatures, in particular in the area of energy production, the *Commission of the European Communities* has recognized the extreme importance of the continued improvement of materials for use at high temperatures.

The Commission is at present assembling in its *Joint Research Centre - Establishment of Petten* (the Netherlands) a White Book which will survey this area and provide criteria for the promotion of research and development in this field of high-temperature materials for industrial use.

To aid in the preparation of this survey, the « *First Petten Colloquium on Advanced High Temperature Materials*: *Technological and Industrial Aspects* » was organized on January 29th and 30th, 1976. Its main purpose was to review, discuss and compare the practical requirements and R and D needs for this area, taking account of the views of the different branches of industry involved in high-temperature technology.

Although originally intended as a small internal meeting with some invited experts, the Colloquium aroused so much interest and attention during its preparation that publication of its proceedings in the open literature appears desirable in order to foster greater awareness of this interdisciplinary forum.

It is therefore gratefully welcomed that the « *Revue Internationale des Hautes Températures et des Réfractaires* » is ready to publish this discussion in two of its regular issues of the year 1976, and it is hoped that wide diffusion of the presented subjects will contribute to the promotion of further progress in this important area.

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(*) Only, *Section 1* is published in that issue (1976, *13*, n° 3, 145-185), of *Revue Internationale des Hautes Températures et des Réfractaires ; Sections 2* and *3* will be published in 1976, *13*, n° 4, 189-263 ; *Section 4* and *List of Participants* will be published in 1977, *14*, n° 1, 5-62.

INTRODUCTION

The purpose of this *Colloquium* is somewhat different from that of ordinary scientific conferences. Its primary objective is to help us to produce guidelines for both fundamental and applied research on materials for applications at high temperatures.

In these days of exploding science and technology, it is unreasonable to expect any individual, or small group of individuals to be competent to assess adequately the many fields of science and engineering endeavour and to define the priority which should be assigned to any specific subject of research. In the field of materials alone, the scope for advancement would appear to be almost infinite, and indeed materials can hardly be considered without taking into account their interaction with other technical fields and disciplines such as design, mechanics, physics, chemistry and above all behaviour in service. When, in addition, we bear in mind the importance and difficulty of constructing a bridge between basic research and engineering technology and application, then the task of providing research guidelines truly becomes a staggering one.

There have always been many reasons and stimuli for exploring the general field of high temperature materials, both in terms of research as well as development. Although the field is not new, it is fair to say that the real impetus for using high temperatures in the critical and advantageous applications with which we are concerned derives from the technological drive of World War II. Some of the most prominent and exciting applications are for propulsion units (turbine and rocket), for high speed aircraft and spacecraft, new and improved methods for energy production including nuclear energy, and metal processing. It has become apparent that materials are one of the major obstacles to efficient utilization of high temperatures and consequently higher efficiencies and to optimised plant design. For example if the gas turbine inlet temperature is increased from 900° C to 1,250° C (for the same specific fuel consumption) the specific power increases by about 30 % — this is certainly impressive. Without adequate high temperature materials and a knowledge of their « personality » we definitely cannot exploit the new theories of science or implement the advanced designs of new technologies.

Having established the importance of high temperatures, we must now look into the basic ways in which we can handle them in practice. The simplest way is obviously to use suitable materials. Where this is difficult or impossible, other techniques, such as cooling, insulation, ablation, etc. must be used, but they suffer from disadvantages of either excessive weight, excessive complexity (as in cooling systems), operating time limitations (as in ablation, useful only for short times and for a single occasion) or limited heat flux (as in heat sinks).

Traditionally, and pragmatically, technology generally precedes science; although there are, of course, many and notable exceptions. In the field of high temperature materials, engineering and empiricism have outdistanced our scientific reservoir of knowledge upon which to build new developments and advances. We are, in fact, somewhat on a plateau of progress in this field, and for major advances, particularly to solve some of the problems already outlined, we must develop new scientific knowledge and understanding. Thus the importance of this Colloquium lies in clarifying and defining the relevant and important scientific issues, and identifying new scientific concepts to permit future investigations to break through the high temperature materials barrier.

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SECTION 1

REQUIREMENTS OF ESTABLISHED TECHNOLOGIES

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 146-159

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MATERIALS SELECTION CONSIDERATION FOR PETROCHEMICAL FURNACE TUBES

By

G. L. SWALES

INTRODUCTION

Increased efficiency is a continuing aim in design for petrochemical furnaces, particularly steam-hydro carbon reformers and steam cracking furnaces for ethylene production, and this aim has in recent years generally resulted in trends to larger scale production units, greater complexity in design and high severity of furnace conditions (temperature, heat flux, pressure etc.). To take full economic advantage of such trends a high level of plant reliability is necessary and consequently increasingly stringent demands are being placed on petrochemical furnace tubes.

This paper outlines some of the major considerations affecting the selection of material for furnace tubes for steam hydrocarbon reformers and pyrolysis furnaces.

REFORMER FURNACES

Catalyst Tubes

Since the trend to high pressure, steam-hydrocarbon reforming, which began in the late 1950's centrifugally cast HK40 (25Cr/20Ni 0.4C) [1] has become the accepted standard for catalyst tubes replacing wrought alloys such as Type 310 heat resisting steel and Alloy 800 previously extensively used for reformers operating at pressures up to about 150-200 psi. HK40, and similar alloys more recently developed to optimise properties of alloys around the 25Cr/20Ni composition range (*e. g.* IN-519) are likely to continue as the predominant materials for a substantial proportion of reforming applications. Nevertheless, increasing use is being made of higher strength, higher alloy materials based generally on the 35Ni/25Cr composition for some ammonia synthesis gas reformers, but more particularly for some higher temperature designs of methanol synthesis gas, oxo alcohol synthesis gas, reducing gas and hydrogen reformers in order to keep tube wall thicknesses below generally accepted limits of 18-20 mm. For example, in hydrogen production, increased hydrogen purity is favoured by higher reforming temperatures whilst in the case of reducing-gas reformers used in direct reduction steel making, higher operating temperature also favours optimum product gas composition and such considerations have led to an increasing usage of various proprietary and non-proprietary alloys based on the 35Ni/25Cr composition for catalyst tubes.

In recent years several surveys based on questionnaires (*e. g.* the *Reformer Information Network* in the USA) have been conducted on reformer catalyst tube life and several papers analysing the results of such surveys have been published [1-7]. Such surveys indicate that the overall failure rate of HK40 tubes, particularly in ammonia synthesis gas reformers, is relatively low but a considerable number of high pressure plants have given markedly inferior performance. The most recent surveys point, however, to improved performance being recorded in many of the plants included in the survey probably due to better operational control.

Failures in catalyst tubes can be broadly categorised as follows:

(1) Nominal compositions of alloys are given in *table I*.

1. Mechanical Failures. — a) *Longitudinal Rupture (in absence of gross internal corrosion).* — This is the most common mode of premature failure associated usually with general or local overheating due to firing conditions, catalyst voids, catalyst deterioration etc. Such failures may possibly be categorised further into stress rupture failures exhibiting marked creep rupture damage (Figures 1 and 2) or where there is gross local overheating, failures may exhibit characteristics more typical of short-term tensile failures. The effect of even moderate overheating on the theoretical life of catalyst tubes is indicated schematically in Figure 3.

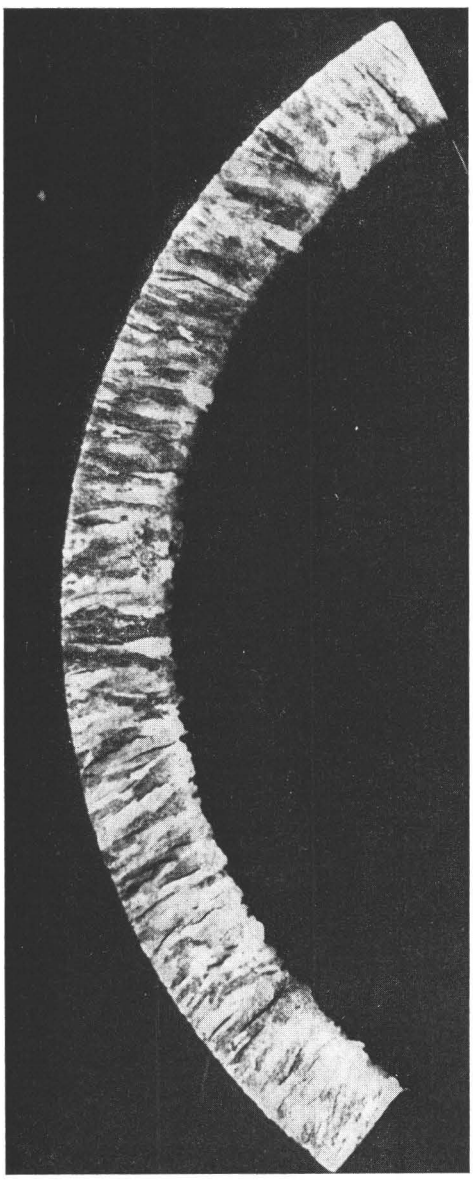

FIG. 1. — *Section through HK40 reformer tube which failed due to overheating, showing multiple creep cracks. Considerable bulging of the tube had occurred in the overheated region.*

b) *Circumferential Weld Failures.* — This mode of failure has been confined to a relatively small number of plants but in some plants has resulted in a high incidence of failure (Figure 4). It is now recognised that

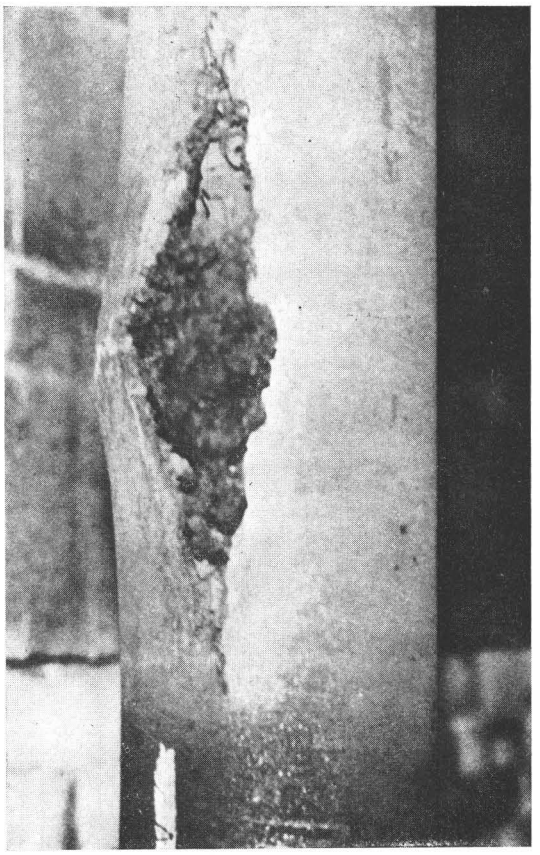

FIG. 2. — *Typical longitudinal rupture failure of reformer catalyst tube.*

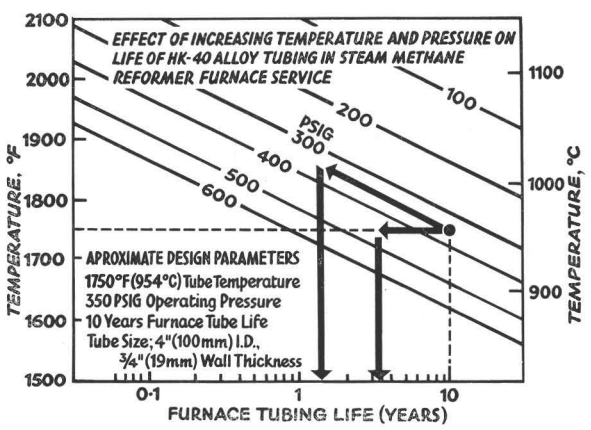

FIG. 3. — *Effect of increasing temperature on theoretical life of HK40 tubing in steam reformer service.*

the stress rupture strength of HK40 welds, particularly metal arc welds, may be as low as 50-60 % of the parent tube material. This mode of failure occurs under conditions where the longitudinal stress due to thermal stressing or design factors is a relatively high proportion (*i. e.* significantly more than 50 %) of the pressure hoop stress on which design is based. HK40 weld metal deposited by TIG welding exhibits somewhat higher stress rupture strength than metal arc welds and this approach has been used where circumferential weld cracking had previously been a problem.

In some early plants circumferential cracking, fre-

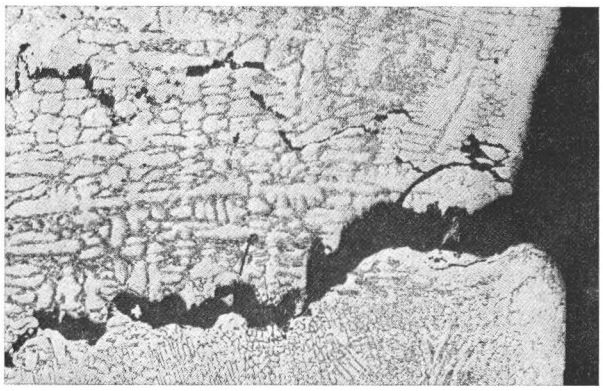

FIG. 4. — *Circumferential weld cracking of a cast HK40 reformer tube after 12 months operation. Weld made with metal arc electrodes of approximately matching composition.*

quently but not exclusively at welds, was experienced due to thermal shock following boiler primes and water ingress into the catalyst tubes (Figure 5). This is nowadays a relatively rare type of failure presumably due to better boiler control.

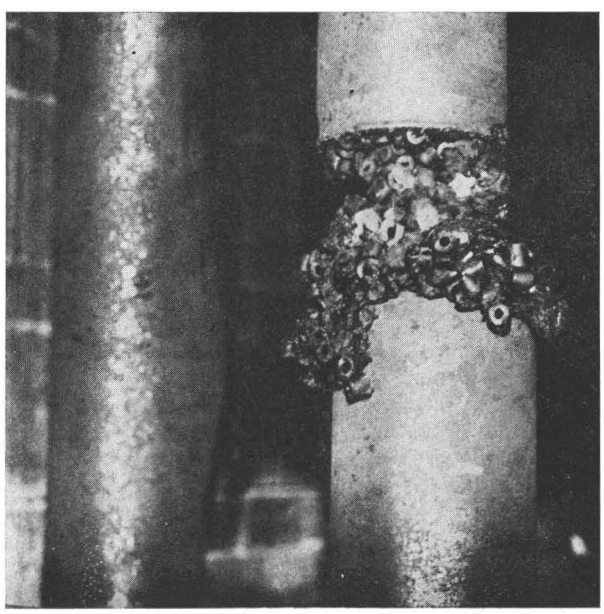

FIG. 5. — *Thermal shock failure of reformer tube near weld due to ingress of boiler water.*

2. Corrosion Failures. — a) *Internal Catastrophic Carburisation — Oxidation Damage.* — A relatively small number of plants has been affected by severe internal localised carburisation-oxidation [8]. Where this has occurred there has been some suggested correlation with abnormally high lead contents in the catalyst tubes.

b) *Stress Corrosion.* — In the mid 1960's there was a spate of failures at the top and bottom extremeties of certain designs of catalyst tubes in some European towns-gas and synthesis gas reforming plants attributable to chloride and caustic stress corrosion cracking respectively in dead zones where condensates could exist. Design changes involving introducing axial entry and exit pigtails instead of the formerly used side entry and exit pigtail designs, eliminating dead zones have largely eradicated stress corrosion cracking problems in catalyst tubes.

Generally speaking, the corrosion and circumferential weld cracking modes of failure, though serious where they have occurred, are relatively uncommon in the industry as a whole and most of the surveys referred to aim at an analysis of factors affecting the more common mode of failure *i. e.* longitudinal rupture.

Several earlier surveys pointed to some possible correlation of frequency of longitudinal rupture with tube thickness, whereas some more recent surveys suggest little or no correlation, and in fact in some of the plants concerned, moderate increases in thickness have apparently improved tube life [5]. Nevertheless, it is generally accepted that injudicious increases in wall thickness are undesirable in that they affect the severity of thermal stress cycles during shut-down and start-up and many designers now start considering alternative catalyst tube material when calculated tube thickness is over about 18-20 mm. Internal machining of tubes to remove the internal zone of shrinkage porosity is now being practised quite extensively for reformer tubes in order to minimise wall thickness. Thermal cycling is recognised as harmful since not only does it affect the stress rupture strength of material, but relaxation of the thermal stresses engendered uses up the alloy's reserve of rupture ductility.

The main mechanical property considerations affecting choice of cast tube materials apart from very important general considerations, such as cost, weldability, castability and oxidation resistance, are long term rupture strentgh, rupture ductility and creep strength. Obviously high rupture strength at the temperature under consideration, is necessary to keep design tube wall thickness below acceptable limits and long term rupture ductility is of importance in the context of the alloy's ability to permit relaxation of high local stresses, repeatedly developed during start-up and shut-down. A certain measure of creep strength is obviously necessary if undue distortion of the tubes and bulging under the pressure stress is to be avoided, but a disproportionately high creep resistance resulting in low creep rates, in relation to other properties, may be undesirable from the view point of obtaining rapid relaxation of high thermally induced stresses.

These considerations were taken into account in studies initially aimed at optimisation of cast alloys around the 25Cr/20Ni composition and culminated in the development of IN-519, a 24 % Cr, 24 % Ni Cr-Ni-Fe alloy containing 0.25-0.35 % C and 1.5 % Nb.

Alternative Catalyst Tube Alloys

IN-519. — Studies at the *International Nickel European Research and Development Centre* indicated that the addition of niobium could significantly improve the stress rupture strength of 25Cr/20Ni cast alloys even at lower levels of carbon. Some adjustement of the nickel, chromium and silicon levels was necessary

TABLE I. — *Nominal compositions of alloys referred to in text.*

Designation	C	Si	Mn	Cr	Ni	Fe	Other
WROUGHT ALLOYS							
Alloy 800	0.1max	0.75	1.0	21	32	Bal.	0.15/0.6Ti
Alloy 800H	0.05/0.1						0.15/0.6Al
INCOLOY 802	0.35	0.5	1.0	21	32	Bal.	
INCONEL 671	0.05			48	Bal.		0.35Ti
CAST ALLOYS							
HK40	0.35/0.45	1.5	1.0	25	20	Bal.	
IN-519	0.25/0.35	1.0max	1.0	24	24	Bal.	1.5Nb
35Ni/25Cr/W	0.45	1.5	1.0	25	35	Bal.	1-3W‡
35Ni/25Cr/Nb	0.45	1.5	1.0	25	35	Bal.	1.0/1.5Nb
HU45	0.45	1.5	1.0	18	37	Bal.	
HT45	0.45	1.5	1.0	15	37	Bal.	
35Ni25Cr/Nb/W	0.45	1.5	1.0	25	35	Bal.	1.0Nb, 1.0W
32Ni/20Cr/Nb	0.1	0.75	1.0	20	32	Bal.	1.0Nb
35Ni/25Cr/15Co/5W	0.45	1.5	1.0	25	35	Bal.	15Co, 5.0W
IN-657	0.1max	0.5+max		49	49		1.5Nb, Low N
30Ni/30Cr	0.45	1.5	1.0	30	30	Bal.	Proprietary additions of minor elements

+ 0.3 % preferred.

‡ *Various proprietary alloys with W in range 1-3 % are included.*

NOTE : *Several of the above alloys are the subject of patents.*

to ensure satisfactory structural stability and the composition range chosen to give the optimum combination of stress rupture and creep strength, rupture ductility and retained low temperature ductility after service exposure is given in Table I.

Figure 6 shows a Larsen Miller plot of the considerable stress rupture data now available and Table II compares the derived mean stresses from this plot with similar figures for HK40 and the ratios of improvement in stress rupture strength at various temperatures for IN-519 over HK40 are indicated.

Comparative stress rupture data for IN-519 and HK40 from 50,000 hour tests has been published [9] and indicates that the advantage of IN-519 over HK40 is maintained over extended testing periods.

Table III compares creep rate data for IN-519 and

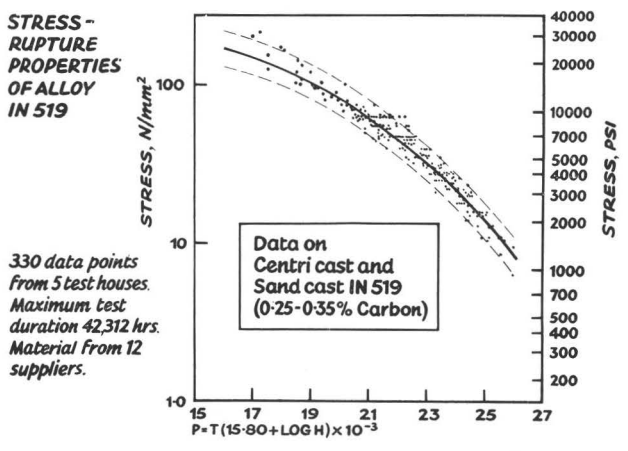

FIG. 6. — *Larsen-Miller stress rupture plot for IN-519.*

TABLE II. — *Comparison of mean derived rupture stress for IN-519 and HK40.*

Temp. °C	Duration (hours)	Mean Derived Rupture Stress IN-519		Mean Derived Rupture Stress HK40		Ratio of Rupture Stress IN-519 / HK40
		psi	N/mm²	psi	N/mm²	
800	1,000	11345	78.2	10392	71.7	1.09
	3,000	9847	67.9	8563	59.0	1.15
	10,000	8331	57.4	6874	47.4	1.21
	30,000	7057	48.8	5587	38.5	1.27
	100,000	5844	40.3	4418	30.5	1.32
900	1,000	6408	44.2	5325	36.7	1.20
	3,000	5261	36.3	4207	29.0	1.25
	10,000	4179	28.8	3220	22.2	1.30
	30,000	3342	23.0	2502	17.3	1.33
	100,000	2580	17.8	1882	13.0	1.37
1000	1,000	3145	21.7	2539	17.5	1.24
	3,000	2425	16.7	1916	13.2	1.26
	10,000	1794	12.4	1391	9.6	1.29
	30,000	1341	9.2	1030	7.1	1.30
	100,000	959	6.6	732	5.0	1.31

NOTE : i) *IN-519 Values from Larsen Miller Plot Figure 5.*
ii) *HK40 Values from Larsen Miller Plot constructed from 99 data points from 4 published and 2 unpublished sources representing 12 heats.*
Data up to 21,700 hours. Larsen Miller constant 14.0.

TABLE III. — *Comparison of creep rates of IN-519 and HK40.*

Temp. °C	Creep Rate %/hour	Stress psi to give specified minimum creep rate IN-519		HK40	
		psi	N/mm²	psi	N/mm²
900	0.001	6205	42.7	6200	42.8
	0.0001	4502	30.0	4500	31.0
	0.00001	2755*	19.0	3200	22.1
1000	0.001	2620	18.1	3400	23.4
	0.0001	1792	12.4	1900	13.1
	0.00001	896*	6.2	1000	6.9

(*) *Extrapolated value.*

HK40. It will be noted that at 900° C creep rates for the two alloys are similar but at 1,000° C the creep rates exhibited by IN-519 are higher than those for HK40. This characteristic combined with the higher rupture strength and creep ductility (referred to later) exhibited by IN-519 suggests that IN-519 possesses a higher ability to accommodate thermal stresses developed during start-up and shut-down than HK40.

IN-519 generally exhibits a higher level of stress rupture ductility than HK40, for example, rupture

tests of 10,000 hours duration on IN-519 at 900° C gave elongation at rupture typically around 8-10 %, compared with 2-3 % for HK40.

IN-519 also exhibits a higher ductility after service exposure than HK40. For example, after 1,000 hours ageing at 800° C, IN-519 shows typically 8-10 % elongation in tensile tests at 20° C compared with the 3-5 % characteristic of HK40.

More care in control of heat in-put in welding IN-519 is necessary than is the case for HK40 to avoid weld cracking and fissuring, but apart from this several thousand welds have been made in fabricating IN-519 reformer tubes without any serious difficulties.

IN-519 exhibits oxidation behaviour comparable with that for HK40 up to about 1,050° C and is considered suitable for reformers with design temperatures up to 1,000° C. Because of the presence of niobium and the lower silicon content, IN-519 gives significantly higher oxidation rates at higher temperatures *e. g.* 1,100° C.

IN-519 is in service in several ammonia synthesis gas, methanol synthesis gas and hydrogen reformer furnaces and is being specified in Europe to an increasing degree. Experience with IN-519 in full scale reformer operation extends up to about 4 1/2 years. Operational experience to date is highly promising, no reports of premature failures yet being referred to the developers of the alloy. In most cases, IN-519 has been utilised with design stresses up to 25 % higher than HK40 resulting in significantly lower wall thicknesses. In a few cases, however, IN-519 has replaced HK40 with only moderate changes in the tube wall thickness, intention being that the alloy's improved properties would provide increased reliability in case of moderate overheating. The data used to compile Table II, which compares the stress rupture properties of HK40 and IN-519, can be re-processed to indicate that IN-519 is capable of with standing a given stress at temperatures of the order of 30° C higher than HK40.

35 Ni/25 Cr Base Alloys. — Several proprietary and non-proprietary cast alloys based generally on the 35Ni/25Cr composition with or without additions of cobalt, tungsten and niobium have been used for reformer catalyst tubes and risers. These alloys show considerable improvement in stress rupture properties, compared with HK40, particularly at temperatures above about 950° C and some proprietary 35Ni/25Cr/Nb alloys appear to have considerably improved rupture ductility. This class of alloy has been used for catalyst tubes in particularly high temperature designs of oxo-synthesis gas and methanol synthesis-gas reformers and also in reducing-gas reformers where HK40 would have resulted in inordinately thick tube walls. However, there are also several cases where alloys of the 35Ni/25Cr/Nb type have been used to replace HK40, with the aim of improving reliability, in ammonia and methanol synthesis gas reformers with design parameters for which the latter would normally be regarded as the standard choice. An alloy containing 35 % Ni, 25 % Cr, 1.25 % Nb is now being specified in Europe for one design of reducing-gas reformer for steel works application involving unusually large diameter catalyst tubes and relatively low pressures but relatively high reformer outlet temperatures (up to about 950° C) and maximum tube wall temperatures probably in excess of 1,000° C.

Catalyst Tubes for Residual Fuel Fired Reformers

In recent years, considerable interest has been shown in the possibility of firing petrochemical furnaces and particularly reformers by residual fuels in view of the potential savings in operating costs which may be achieved.

Smolen [11] has reviewed some of the problems involved in firing petrochemical furnaces with residual fuels. One of the major problems with fuels containing appreciable amounts of vanadium, for example more than about 10 ppm, is fuel ash corrosion of the furnace tubes. There has been very little practical experience of firing high temperature petrochemical furnaces as distinct from oil refinery heaters, but there have been one or two reports of some usage of residual fuels in reformers with resultant severe tube corrosion problems.

In recent years there have been some material developments which give some promise of possible application to petrochemical furnaces fired by residual fuels, for example low and medium pressure reformers. High chromium chromium-nickel alloys *e. g.* containing 50 % Cr, have been successfully used to mitigate oil ash corrosion problems in oil refinery heaters, marine and land based boilers [12]. These alloys show vastly improved resistance to oil ash corrosion compared with 25Cr/20Ni alloys. As originally developed the basic

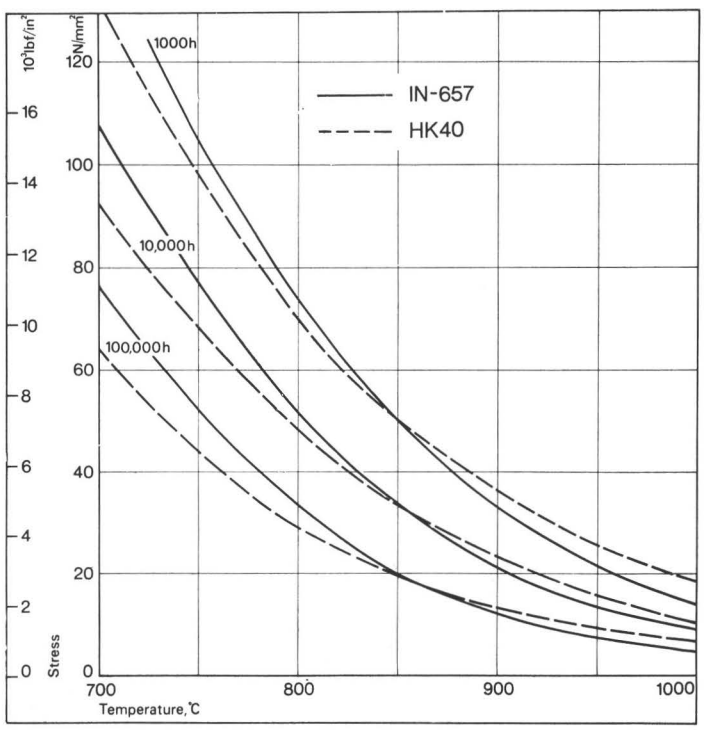

FIG. 7. — *Comparison of mean derived rupture stresses for IN-657 and HK40 to give lives of 1,000, 10,000 and 100,000 hours.*

50Cr/50Ni alloy had poor stress rupture properties but a recently developed niobium containing modification (50Cr/50Ni, 1.5Nb) has rupture strength equal to HK40 at temperatures up to about 900º C [12] and only slightly less between 900 and 1,000º C (Figure 7). This alloy designated IN-567 and produced by several licenced foundries has been used extensively for oil fired refinery heaters in recent years and centricast IN-657 tubes are under field trial in petrochemical furnaces. Standard 50Cr/50Ni alloy tubes behaved satisfactorily from the corrosion view point in a low severity ethylene furnace fired during a four-year run for much of the time with a 40 ppm vanadium fuel oil.

Another interesting development which has possibly some relevance for low and medium pressure reformers fired by residual fuel is a duplex wrought tube designated Incoclad (*) 671/800H which consists of a tube of Incoloy (*) Alloy 800H with an external layer of Inconel (*) Alloy 671, a 50Cr/50Ni, 0.35 % Ti alloy [13].

REFORMER OUTLET PIGTAILS

Outlet pigtails connecting reformer catalyst tubes to manifolds are a critical part of the majority of reformers, though some important designs in extensive use for ammonia synthesis-gas reforming, do not involve pigtails, the catalyst tubes being directly connected to internal headers to form « harps ». Even with the latter type of design, pigtails are sometimes incorporated to permit tube isolation by « pigtail nipping ».

Cold drawn and solution annealed Alloy 800 to ASTM B407 Grade 2, has been the standard choice for pigtails for a number of years. More recently Alloy 800 with tighter carbon control designated Alloy 800H which has a higher range of rupture strength, has substantially replaced the B407 Grade 2 for high temperature applications. Substantially higher design stress is accorded to Alloy 800H in ASME Code Case 1325-7 (November 1973) compared with B407 Grade 2 and will be referred to later.

Although Alloy 800 Grade 2 has generally given excellent service in this critical application some plants have experienced pigtail problems over the years to varying degrees, whilst others have had no problems [7]. Where pigtail problems have occurred they have been generally associated with design, operation and fabrication rather than the pigtail material itself:

a) **Design and operation factors.** — A substantial proportion of failures appear to have been associated with design. Several cases of premature failure attributable to thermal fatigue have been recorded: this has occurred for example in certain designs of furnace where relatively short, straight pigtails have been used in conjunction with certain tube configurations and where relatively large numbers of shut-downs and start-ups have occurred.

b) **Composition factors.** — Abnormally low carbon contents in conjunction with titanium and aluminium contents at the extreme low end of the specification range, together with non-standard heat treatments, seem to have been responsible for several cases of premature creep failure of Alloy 800 type pigtails in several European plants in the mid-1960's. Replacement by Alloy 800 to SB407 Grade 2 overcame such problems at these plants.

c) **Heat treatment.** — In a number of early plants mill annealed Alloy 800 tubes (Grade 1) were specified instead of solution annealed-material (Grade 2) resulting in premature failure due to creep. Mill annealed tubing with its finer grain size has substantially lower stress rupture properties than coarser grain, solution annealed material. In the new nomenclature implied by ASME Code Case 1325-7, Alloy 800H will replace the former Grade 2, whilst the mill annealed material, formerly Grade 1, for use at temperatures where short term tensile properties are the controlling criteria will be designated Alloy 800. It is generally recommended that pigtails for service at temperatures above 1,500º F (815º C) are re-solution heat treated after bending to avoid any possibility of recrystallisation occurring in service, resulting in possible small grain size and consequently lower creep rupture strength [14].

d) **Weld Problems.** — Failures at welds joining pigtails to catalyst tubes and headers have been responsible for shut-down at several plants. Inferior weld quality and the use of weld metals with insufficient strength have generally been responsible. Higher strength weld metals are now available for welding Alloy 800H and will be referred to in more detail later in connection with reformer manifolds.

e) **Carburisation.** — Carburisation of pigtails have been reported in a few plants, often, but not exclusi-

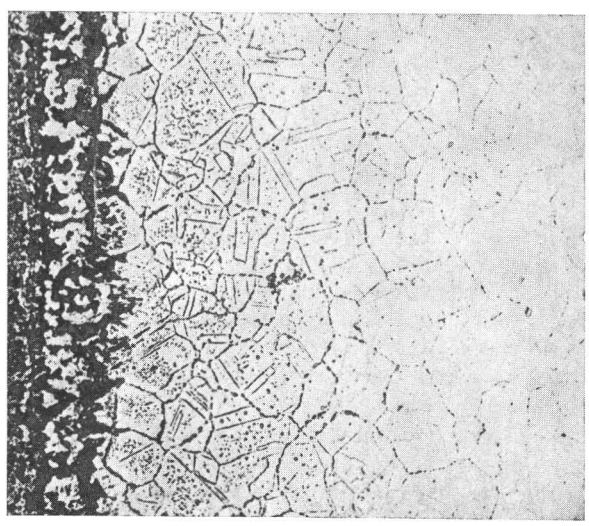

FIG. 8. — *Carburised Alloy 800 Grade 2 pigtail associated with overheated tube.*

(1) Trade Mark.

vely, in pigtails associated with tubes which have been running too hot for some considerable period (Figure 8). In addition to temperature, certain process parameters such as steam/feed ratio may obviously have an influence on the propensity to carburisation, although these factors are not completely understood. There have been cases where carburisation of the pigtail prevented successful isolation of tubes by pigtail-nipping, a technique which otherwise has been very sucessfully used in many European plants to avoid shutting-down a reformer because of a leaking tube or an obviously over-heated tube. Some plants employing pigtail-nipping for tube isolation monitor carburisation of pigtails by magnetic methods and when carburisation has reached a certain level short lengths of new pigtail tubing are inserted to permit satisfactory pigtail-nipping if it becomes necessary during subsequent operation.

Reformer Manifolds

Both wrought and cast alloys have been used for reformer manifolds but following a number of failures of high carbon cast alloy headers (HU 45, HT40, HK40) in the mid 1960's, attributable to low retained ductility, there was a marked trend back to the use of wrought material particularly Alloy 800 Grade 2, which had a long history of successful applications in many plants, both for external and internal manifolds. Subsequently low carbon cast alloys with good retained ductility over a wide temperature range were developed by heat resistant foundries and have been used in a number of reforming plants and other petrochemical piping applications in Europe.

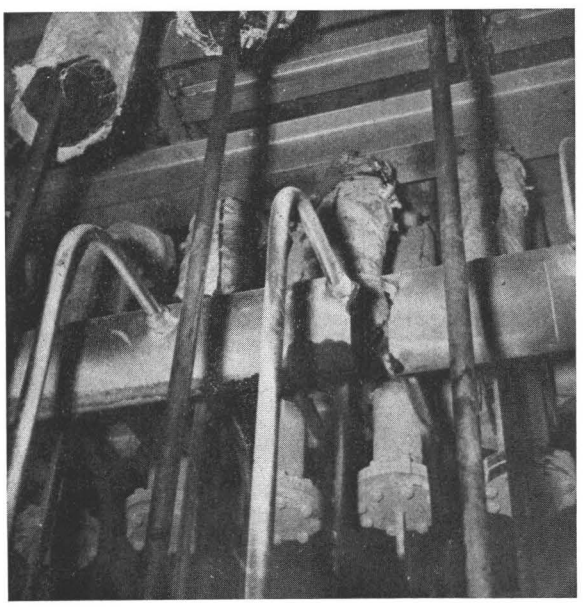

FIG. 9. — *Thermal shock failure of reformer manifold in high carbon 37Ni 18Cr cast alloy due to water ingress following a boiler prime.*

Cast high-carbon alloys such as the 0.45 carbon 37Ni/18Cr alloy have good ductility at high temperatures but below about 650°-700° C the alloy has relatively low ductility following service exposure. Several failures of cast 37/18 high carbon alloy headers occurred particularly, but not exclusively, in towns gas reforming plants where header temperatures tended to be relatively low (Figure 9). Many of these failures were due to thermal shock following boiler primes which caused ingress of water into the catalyst tubes [15]. Direct cast equivalents of Alloy 800 *i. e.* low carbon 32Ni/20Cr alloys were introduced by some foundries for header applications since these alloys have good retained ductility, but experience was not good due mainly to welding problems and in particular relatively poor creep rupture ductility. The addition of about 1 % niobium to cast 0.1 carbon 32Ni/20Cr alloys has, however, an extremely beneficial effect, improving the weldability and creep-rupture ductility to a remarkable degree and increasing the stress rupture strength to a level even higher than the high carbon 37Ni/18Cr alloys previously used for manifolds. The low carbon 32Ni/20Cr/Nb alloy has been used in the last few years in a number of European reforming plants with reported good results.

Reference has been made earlier to improvements in stress rupture properties of Alloy 800 by tighter carbon control and the consequent introduction of Alloy 800H (ASME Case 1325-7) and this is of particular significance for reformer manifolds. The main requirement for this grade is a minimum carbon content of 0.05 % (range 0.05-0.1 %) which in conjunction with solution annealing to give the grain size of ASTM 5 or larger gives significantly higher levels of stress rupture properties than represented by the formerly used ASME SB407 Grade 2.

Table IV compares representative 100,000 hour stress rupture properties and ASME design stresses for Alloy 800 (SB407 Grade 2) and Alloy 800H (Code Case 1325-7).

Although Alloy 800 Grade 2 pipe when specified in the correct solution treated condition has rarely given any problems, there have been problems with welds in headers and pigtail/header connections [7]. Some of the weld metals previously used for welding Alloy 800 (Grade 2) have significantly lower stress rupture properties than the parent tube in certain temperature ranges. Inconel electrode 182 which was frequently chosen because of its better operating characteristic is an electrode which was shown by experience to have inadequate rupture strength. Problems with welds in headers have been significantly reduced by using Inco-Weld (1) A electrodes for metal arc welding and Inconel filler metal 82 for inert gas welding, in preference to Inconel electrode 182. More recently, stronger weld metals, Inconel electrode 112 and Inconel filler metal 625 have been introduced for use in conjunction with Alloy 800 Grade 2 and Alloy 800H for service temperatures above about 850° C and employed in

(1) Trade Mark.

recent years to a considerable extent for welding headers and pigtails with high design temperatures. The 10,000 hour stress rupture strength of these deposits matches that of Alloy 800H up to about 925° C. Table V compares the stress rupture strentghs of deposits made with the previously mentioned consumables.

TABLE IV. — *Comparison of rupture strength and ASME design stresses for Alloy 800 (SB407 Grade 2) and Alloy 800H.* (ASME Case 1325-7).

Temperature		Alloy 800 (SB407 Grade 2)				Alloy 800H (ASME Code Case 1325-7)			
		Rupture Strength 100,000 hrs.		Design Stress ASME Section VIII Div.1 1974* Edition		Rupture Strength 100,000 hrs.		Design Stress ASME Code Case 1325-7 1973	
°F	°C	psi	N/mm²	psi	N/mm²	psi	N/mm²	psi	N/mm²
1200	693	13,000	90	7900	54	13,000	90	8400	58
1300	704	6,800	47	4600	32	8,700	60	5400	37
1400	760	4,000	28	2800	19	5,000	34	3600	25
1500	816	2,500	17	1700	12	3,600	25	2500	17
1600	871	1,600	11	-	-	2,400	17	-	-
1700	927	900	6.2	-	-	1,500	10	-	-
1800	982	620	4.3	-	-	800	5.5	-	-

(*) *Deleted in ASME Winter Addenda 1974.*

TABLE V. — *Rupture strengths of welding consumables for Alloy 800.* (all weld metal specimens).

Welding Consumable	Temperature		Stress psi for Rupture in		
	°F	°C	1,000 hr.	10,000 hr.	100,000 hr.
INCO-WELD A Electrode	1000	536	51,000	39,000(E)	-
	1200	648	24,500	16,000(E)	-
	1400	760	11,090	7,100(E)	-
	1600	871	3,650	1,900(E)	-
	1800	982	900	-	-
INCONEL Filler Metal 82	1000	536	52,000	47,000(E)	-
	1200	648	27,500	20,500	-
	1400	760	11,500	8,300	-
	1600	871	3,500	1,750	
	1800	982	1,250	570	-
INCONEL Electrode 182	1000	536	50,000	41,000	-
	1200	648	22,500	14,500	-
	1400	760	7,500	4,400	-
	1600	871	2,150	1,150	
	1800	982	820	410	-
INCONEL Filler Metal 625 and INCONEL Electrode 112	1000	536	-	-	-
	1200	648	42,000	34,000	28,000(E)
	1400	760	15,500	12,000	9,200(E)
	1600	871	6,800	4,300	2,800(E)
	1800	982	2,000	870(E)	390(E)

(E) = *Extrapolated*

ETHYLENE FURNACES

Ethylene, one of the most important petrochemical intermediates, is produced principally by steam-cracking of various hydrocarbon feedstocks, such as ethane, naphtha and gas oil in tubular furnace coils at temperatures generally in the range 750-1,000° C. The cracking furnaces represent about 20 % of the total plant cost and consequently selection of tube materials is a critical factor affecting initial cost and ultimate operation costs linked to downtime, maintenance and replacement.

Since the early sixties the capacity of ethylene plants has increased typically from around 100,000 tonnes p. a. to 350-500,000 tonnes p. a. The main trends in cracking process design in this period have been towards higher severity cracking to maximise ethylene yield, involving high cracking temperatures, shorter residence time and high heat flux. Material selection has followed such trends to higher temperatures.

The early low and medium severity furnaces had mainly horizontal tube coils supported by relatively massive tube supports which had to withstand the high temperatures in the radiant zones of the furnace. As operating conditions became more severe, with initial trends to higher severity cracking, selection of material for tube supports became increa singly difficult and modern high severity furnaces have vertically disposed tube coils with coil supports arranged in relatively cool zones of the furnace.

To obtain high heat flux in short residence time heaters and at the same time minimise tube temperature, there has been a trend to lower diameter cracker tubes and tube internal diameters of 50-55 mm are now common which approaches the current minimum practical diameter limit for high integrity centrifugally cast tube production. At least one recent design of ultra-short-time residence heater involves tube diameter of around 40 mm and if such designs become more common wrought tubes or « weld-formed » cast tubes (referred to later), will have to be considered; it is understood that one such prototype plant with weld-formed tubes is in operation in Japan.

Cracker Tube Materials

In the earlier low and medium severity furnaces wrought material such as AISI Type 304 stainless steel (18Cr/10Ni), Type 310 (25Cr/20Ni) and Alloy 800 Grade 2 were used but with the trend to vertical furnaces centricast tubes in HK40, HL40 and some 35Ni/25Cr base cast alloys were generally specified for strength reasons. HK40 has been used in a large number of plants and in more recent high severity units a combination of HK40 and 35Ni/25Cr base alloys has been adopted, the higher alloy being used for the hotter legs of the coil. In the last three or four years there has been some resurgence of usage of wrought material in North America, particularly a 0.35C 32Ni/20Cr alloy, designated Incoloy Alloy 802, whereas in Europe centricast tubes have been predominant. As a broad generalisation for centrifugally cast tube cracker coils, HK40 is specified for temperatures up to about 950° C-1,000° C and for higher temperatures various proprietary alloys of the 35Ni/25Cr/W/Nb; 35Ni/25Cr/W and 30Ni/30Cr type are used.

a) **Carburisation.** — Carburisation has long been recognised as an important factor in the performance of ethylene furnace pyrolysis tubes [18, 19]. Carbon contents of up to about 4.5 % have been measured on the carburised inner surfaces of cracker tubes, and in addition to the effect on properties, volume changes associated with carbon pick-up and differences in thermal expansion coefficient between carburised and uncarburised zones can impose a high level of tensile stress on the underlying carburised zones. Fissuring seems to be initiated adjacent to be carburised layer and these fissures propagate to the outer wall and lastly to the inner wall. Oxidation of the carburised zone during for example thermal decoking can result in metal loss. Figures 10, 11, 12 and 13 show examples

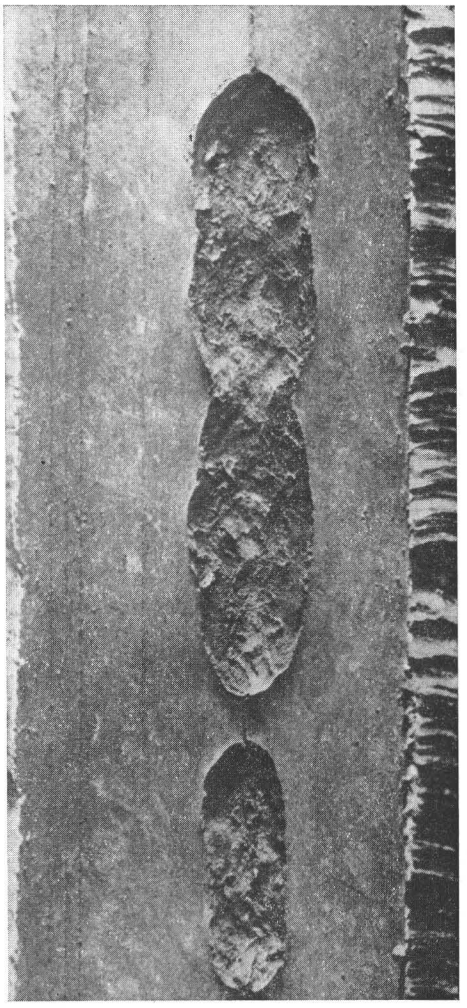

FIG. 10. — *Localised carburisation-oxidation pits in a Type 310 furnace tube in medium severity gas oil cracker (Note the rolling « seam » at the major axis of the pits suggesting the possible importance of surface condition in initiating carburisation).*

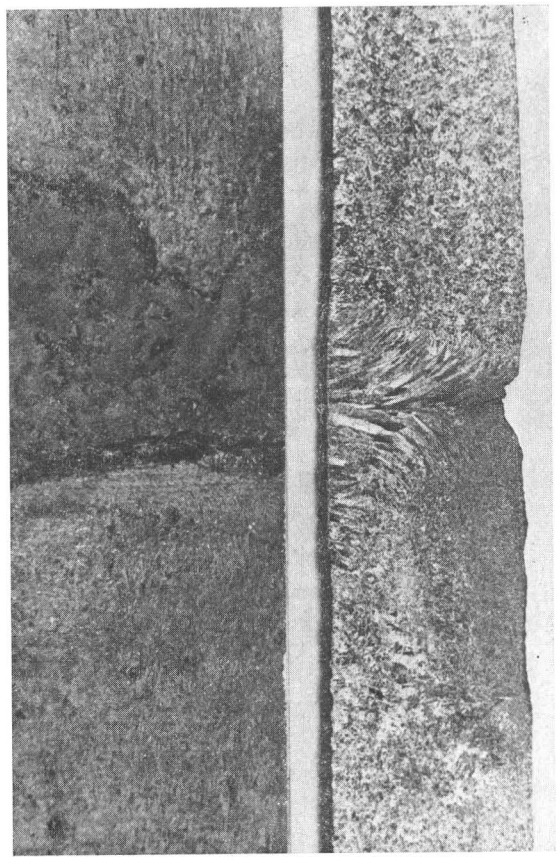

FIG. 11. — *Localised carburisation at an under-penetrated weld in a pyrolysis tube from a medium severity ethylene furnace.*

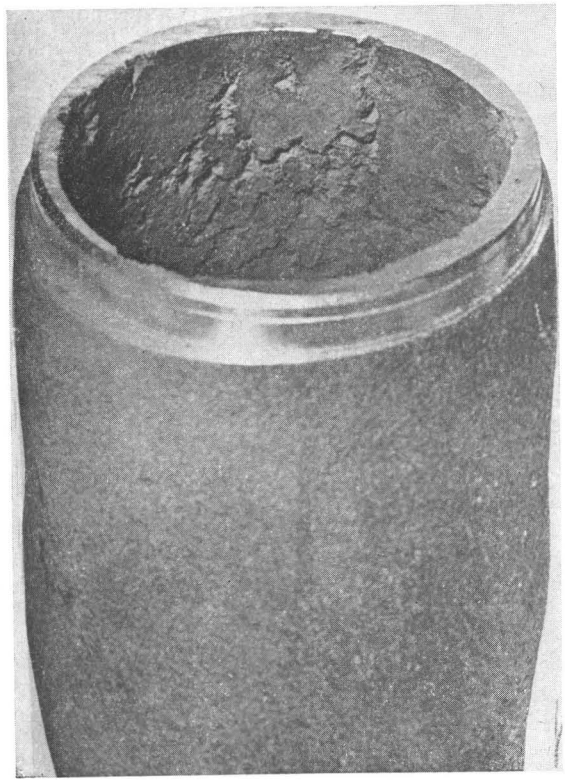

FIG. 12. — *Carburisation of HK40 cracker tube from a high severity ethylene furnace. Note internal wastage and bulging.*

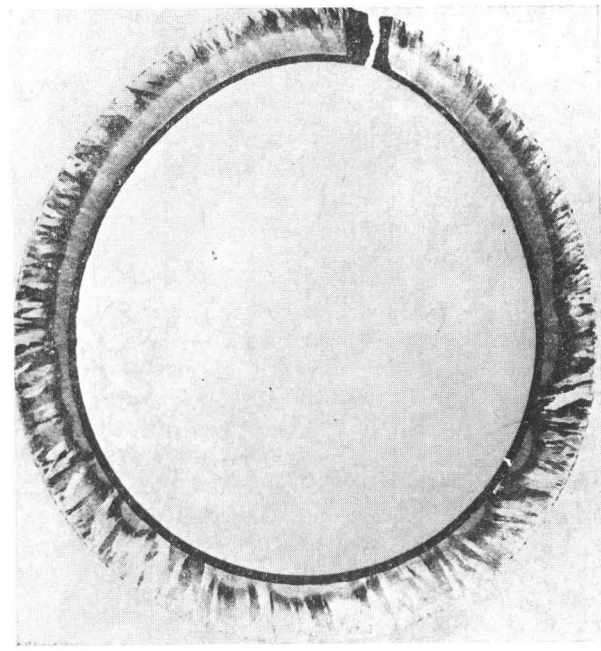

FIG. 13. — *Irregular carburisation in an HK40 tube from a high severity heater due to an uneven temperature distribution resulting in bulging and creep failure.*

of carburisation in ethylene furnace tubes. In low and medium severity furnaces carburisation is frequenly very localised at hot spots and zones of turbulence, where local coke build-up occurs and subsequent decoking results in uncontrolled burning of the coke deposit and excessive local temperatures. In higher severity cracking, because of the higher general temperatures, carburisation may be much more widely distributed though varying in depth according to the temperature profile (Figure 12).

Experience in numerous plants has demonstrated the importance of internal tube surface finish on carburisation. Considerable improvement is obtained by internal machining to remove the internal bore microporosity of cast tubes (Figure 14). Much of the obtainable benefit appears to accrue from removing the bore microporosity and providing a machined surface of 64-128 RMS, a higher degree of surface finish having little additional beneficial effect. Such findings have led to bore-machining becoming an established procedure for centricast tubes for ethylene service. Hubert and Thuillier [19] have published results on field trials in an ethylene furnace of various candidate cast alloys in the machined and unmachined condition in the temperature range 870-1,060° C. Some of the results obtained at temperatures around 1,000° C are summarised in table VI. The same authors have suggested, on the basis of laboratory tests, that there is a significant difference between the carburisation behaviour of cast tubes with a columnar structure compared with those having an equiaxed structure of centricast tubes. Weld-formed tube produced by a combination of continuous casting and electroslag metal deposition does have characteristically columnar grains at the bore (Figure 15) and as indicated earlier, can be produced in smaller diameters than centricast tubes. Although weld-

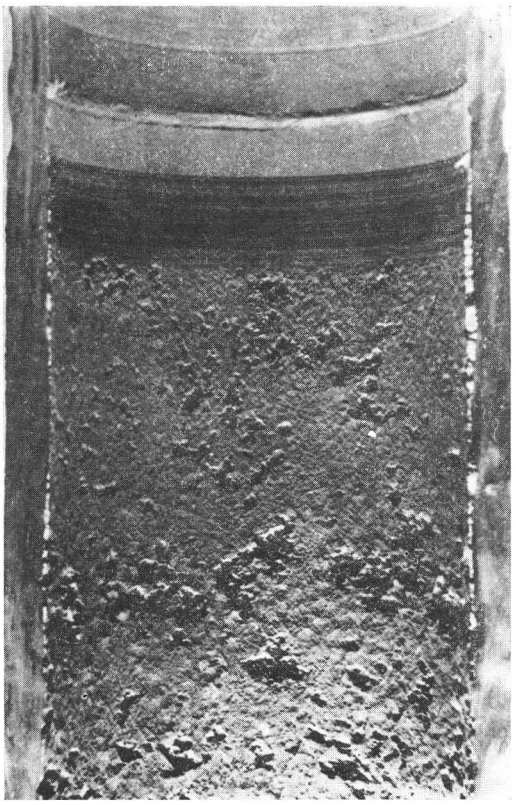

FIG. 14. — *Carburisation of an HK40 ethylene furnace tube. Note the severe damage on the unmachined part of the tube and the absence of attack at machined zone near weld.*

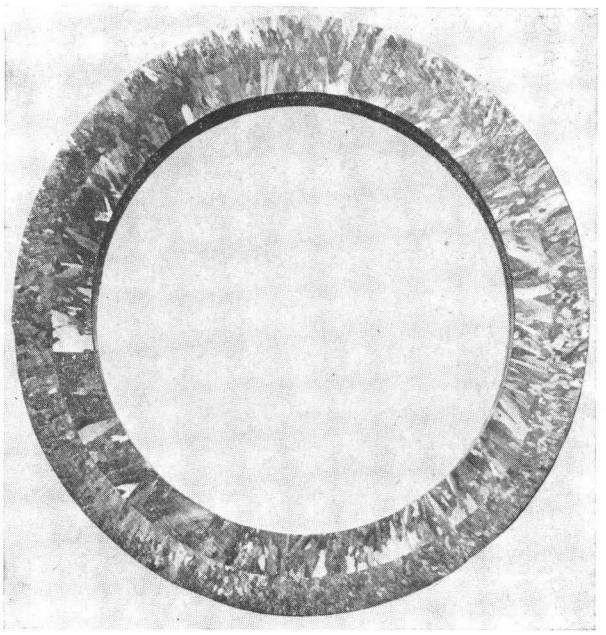

FIG. 15. — *Macro section of HK40 « Weld-Formed » tube.*

formed tube is understood to be in service in at least one high severity cracker in Japan, because of limited availability and lack of wide spread experience, it is unlikely to be a major competitor to centricast tube outside Japan in the foreseeable future.

A considerable amount of laboratory testing on candidate alloys for ethylene pyrolysis tubes using pack carburising, gas carburising and salt bath carburising has been done [17, 19, 20] and whether or not such tests have any relevance to actual carburisation in ethylene furnaces is often hotly debated. They have some value, however, as screening tests in alloy development and generally give the following indications as to the effect of composition. Silicon is perhaps the most potent alloying element in reducing the depth of carburisation, but restrictions placed on silicon content in many heat resisting alloys for mechanical property and weldability considerations limit the extent to which this approach may be adopted.

Nevertheless, the silicon content stipulated in many HK40 specifications for ethylene furnace tubes is

TABLE VI. — *Carburisation of a series of cast alloy tubes from field trials in high severity furnace* (Hubert and Thuillier [19]).

Distance from Internal Surface (mm)	Increase in Carbon Content %							
	25Cr/20Ni		35Ni/25Cr/W		35Ni/25Cr/Nb		35Ni/25Cr/Nb/W	
	as-cast	machined-bore	as-cast	machined-bore	as-cast	machined-bore	as-cast	machined-bore
1	1.75	0.11	1.95	0.19	0.6	0.07	0.2	0.04
2	1.6	0.13	1.9	0.21	0.5	0.11	0.15	0.05
4	1.1	0.10	1.3	0.16	0.15	0.06	0.1	0.03
6	0.65	0.07	0.3	0.09	0.05	0.04	0.05	0.02
8	0.3	0.05	0.15	0.05	0.05	0.03	0.05	0.01
10	0.1	0.04	0.05	0.02	0.05	0.02	0.05	nil

All cast tubes exposed for 7,000 hours. Temp. $\simeq$ *1 000° C.*

higher than for reformer tube applications. Substantial increases in nickel and chromium appear to reduce the carbon gradient and at the same silicon content 35Ni/25Cr base alloys show better carburisation resistance than 25Ni/20Cr alloys. Also, carbide stabilising elements such as niobium and tungsten appear to have some beneficial effect. Most of the proprietary cast alloys being offered as improvements on HK40 for pyrolysis tubes are based on the 35Ni/25Cr composition with additions of niobium, tungsten, or both. Most of the laboratory studies done on carburisation have been devoted to comparisons of alloys in terms of maximum carbon content and depth of carburised layers and there has been very little attention given to the properties of partly carburised tubes, to determine for example if materials with high creep ductility can withstand more carburisation damage than lower ductility high creep strength materials.

b) **Mechanical Property Considerations.** — Although carburisation is without question a major factor affecting the life of ethylene furnace tubes, final failures are generally by creep-rupture and consequently other characteristics of the tube material in addition to depth and gradient of carburisation, must have some influence on tube life *e. g.* rupture strength, creep ductility-stress relaxation characteristics, properties of carburised layers etc.

Closer attention been has given by some ethylene furnace designers in recent years to the properties of tube materials in relation to their ability to accommodate, by quick relaxation, the stresses developed in the coil in the various phases of operation (*i. e.* start-up, pyrolysis, thermal decoking and shut-down), their stress analysis studies involving consideration of combined creep and low cycle fatigue [21, 22]. The ability to quickly relax high thermal stresses and stresses imposed by carburisation during pyrolysis and decocking implies material should not have too high a creep strength (*i. e.* a relatively high creep rate to permit quick relaxation) but a high creep ductility. At the same time a sufficiently high rupture strength is necessary for economic design and the creep strength should not be so low as to result in excessive distortion of the coil or bulging under the pressure stress. Clark [18] has reviewed this approach in the context of newly developed wrought materials, *e. g.* 0.35 carbon, 32Ni/20Cr-Incoloy Alloy 802 which has stress rupture properties of the same general order of HK40 but much lower creep strenght and higher creep and tensile ductility, and he refers to some field experience. Such concepts have led to the specification of wrought alloys, particularly Incoloy Alloy 802 during the last three or four years for ethylene furnace coils, both for replacement and new installations, in a considerable number of plants in the USA and for six or seven plants outside the USA. In Europe, cast alloys, particularly HK40 and proprietary 35Ni/25Cr alloys have been predominant in high severity furnaces, the former for maximum tube temperatures up to about 950º C and the latter for higher temperatures. Relatively high creep rupture ductility can also be developed in certain cast heat resisting alloys and alloy development programmes of centricast tube foundries have been directed at optimising rupture strength, creep rate, creep ductility and carburisation resistance etc.

Although considerable field testing has been carried out in many plants, little of this information is generally released since tube behaviour is intimately connected with detailed ethylene process design, feedstocks, mechanical design etc., which is highly proprietary information. There appears to be relatively little scope for collaborative surveys on tube performance such as have been carried out on reformers.

Convection Section Tube Materials

Wrought alloys are used extensively for convection section tubing in ethylene furnaces; in earlier plants Type 304 and Type 321 tubing was used in the hotter convection zones but with trends to higher convection section temperatures, Alloy 800 H is being increasingly used for lower convection section tubes and « crossover » tubing connecting the convection and radiant sections. Some problems with thermal fatigue cracking of crossover tubing near steam inlets have been reported in one or two plants, this being due to ingress of wet steam. Such problems have generally been resolved by design modifications.

Transfer Lines and Furnace Outlet Piping

The cracked gases from the furnace coil have to be rapidly quenched in order to reduce the temperature in order to minimise secondary cracking reactions which could reduce the ethylene yield. This is accomplished in transfer line heat exchangers. The furnace outlet connections and the transfer lines between the furnace and quench exchangers are relatively highly stressed systems and may be subject to thermal shock and thermal cycling, placing severe demands on the material of construction. Materials for these piping systems must have good stress rupture properties combined with high ductility over a wide range of temperatures even after extended exposure at service temperatures.

Thermal fatigue cracking near purging steam and decoking steam inlets has on occasion caused failure, particularly where ingress of wet steam has occurred Careful design and inspection are obviously important requirements in connection with transfer lines.

In a number of European plants of one design, built in the early/mid sixties HK20 and HK40 cast alloys were used for pipe and fittings in the furnace outlet and transfer ne systems and several failures occurred, in some cases after only relatively short periods of service generally ascribable to inadequate creep rupture ductility at the operating temperature and low retained ductility at the lower temperatures encountered during start-up, decoking and shut-down. Either wrought Alloy 800 Grade 2 or cast low carbon 32Ni/20Cr/Nb alloy were used for replacements in the plants referred to on account of their higher ductility, in general solving the previous problems. One or other of these alloys, depending on detailed design considerations, is now the standard choice for furnace outlet and

transfer line piping systems in most furnace designs and providing care has been taken in design and operation to avoid severe thermal fatigue conditions, their performance in this difficult application has been generally good.

CONCLUSION

Some of the main considerations for selecting materials for furnace tubes in steam-reforming and steam-cracking have been outlined in the context of improving reliability and meeting the demands of ever developing process design technology. Whilst established cast and wrought furnace tube materials *e. g.* standard chromium-nickel cast steels, Alloy 800 H and the AISI 300 series of heat resisting steels will continue to satisfy a large proportion of petrochemical furnace requirements for the foreseeable future, several newer proprietary and non-proprietary alloys are now in moderately extensive service, and others are being evaluated to meet some of the more stringent material requirements likely to result from future developments in high temperature petrochemical furnace technology.

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Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 160-162

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HIGH TEMPERATURE MATERIALS REQUIREMENTS FOR THE CHEMICAL INDUSTRY

By

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As a generalisation in chemical plants, process streams, usually under pressure, are heated to reaction temperature. It is then sometimes necessary to hold them at fixed temperatures in vessels to allow the reaction to take place, and then it is necessary to cool the product. We can divide the subject therefore into Heaters, Vessels and Coolers and perhaps one ought to add Transfer Lines. There are some processes which use kilns, these however will not be discussed.

GENERAL VALUE CRITERION

There is no weight limitation on chemical plants, which means that in the simplest case enhanced creep resistance is valuable only if it provides us with equipment which costs less than that which can be built from an inferior material. This is a tough demand for the metallurgist since the alloying elements he uses to obtain creep resistance are expansive, and costs tend to increase more rapidly than creep properties. Fabrication costs also tend to be high in the case of high alloys.

VESSELS

Perhaps it would be best to discuss vessels and transfer lines first because in these there is no significant heat trasnfer across the metal thereby simplifying some of the problems. Insulation is necessary for heat conservation and it is generally possible to install it internally without great difficulty. The significance of this is when temperatures are such that anything other than relatively simple and inexpensive alloys would have to be considered the insulation is placed internally, and the vessels and the lines are then built out of carbon steel.

By this means, quite large vessels are frequently built for service at 20-30 bar and up to 1,000° C. These have proved to be very reliable in service. The design of such vessels does call for special knowledge and experience, but the refractory used for internal insulation is not sophisticated or expensive and is placed in position by reasonably conventional means. Were there a need for higher temperatures and pressures, this could be handled in the same way, and there is no obvious problem requiring research on materials at the high temperature end as far as vessels are concerned. There are problems however at intermediate temperatures where there is no internal insulation. In these cases most equipment is designed on creep criteria and according to codes. In these vessels it is extremely difficult to know how to treat branches and other features where the stress pattern is complex both because of the geometry and the thermal stresses present, and especially so since welds are normally also present.

This is a problem on which engineers and metallurgists are working, but perhaps there is one aspect which may call for further study. In practice vessels are periodically inspected, and warning of potential failure is found during such inspections. It may be that present NDT techniques are all we actually need, but if the metallurgist could come up with techniques which are cheaper or which provide us with better information, there would obviously be interest shown. To understand what is required, it must be appreciated that the ins-

pection costs are very high because it is necessary to shut down plants, and the costs involved are very high. It is moreover, necessary to open up equipment, clear it for entering, clean it and then inspect it. The cost of the actual inspection is significant by comparison to the other costs, and the need is to consider whether the whole operation can in some way be reduced without, however, reducing safety standards in any way.

HEATERS

Turning now to heaters, the problems here are different because in this case the metal cannot be protected from temperature and is exposed both to creep and environmental attack. Reformers and crackers work up to 900° C or even more and clearly for these one has to use the higher alloys since it is impractical to obtain a reasonable life by simply increasing the thickness of the tubes. Mr. Swales has dealt with some of the problems met in this area but perhaps it is worth saying again that within limits weight is not important. Since such equipment is basically expendable the life expectancy is the important factor worth paying for. It is not easy to generalise on the value placed on extra life because the position differs from case to case. Basically, because of discount cash considerations, people might be prepared to pay, for instance, some 10-15 % more for an expectancy of ten years, instead of five. This gives the metallurgist little scope for expensive alloying element additions beyond the absolutely necessary. This is why the practice is to use high carbon cast alloys because carbon is a cheap alloying addition and castings are cheap. It so happens that this family of alloys would now be difficult to beat technically with forged alloys but perhaps this was unexpected when they were first introduced. What is strange is that the potential offered by these alloys for other duties is not being examined.

There are two inter-related technical problems which perhaps do need further study. Since there are relatively large temperature gradients across the walls of tubes, especially during start-up and shut-down conditions, there are appreciable thermal stresses across the walls of tubes and some of these will relax and leave behind complex stress patterns. We do not know, with certainty, how best to treat the problem mathematically nor do we know whether the information would be useful or how to use it. The information would be of no help in itself unless we could heat or cool a furnace to minimise the effect on life expectancy. It is unlikely that with the limitations available on starting or shutting down a plant anything significant can be done. However there could be other benefits.

Whilst I have said it is not worth paying a great deal more money for an alloy which is marginally stronger than another for reasons already explained, given two alloys offered at the same price one naturally would select the strongest. Therefore from a suppliers point of view a small difference between his alloy and that of his competitors is a very important matter, because it makes all the difference between selling or not selling the product. The unfortunate thing is that, given temperature cycling, it is not at all easy to know what combination of properties does give the longer life, and it may well be that the « stronger » alloy is not the best. The problem is therefore to establish what is « best ».

The related problem is that of welds. In this region we have mis-match of properties and whilst, through experience, it has been established how to make welds which do not often fail prematurely in service, surprises do sometimes occur. It is probably fair to say that no one is absolutely certain how to treat the subject either theoretically or experimentally without doing the very expensive and long duration simulation tests which make progress slow. Whether theory and calculating techniques are sufficiently advanced to allow reliable predictions to be made at present is not clear, but if they are not, perhaps there is another approach. Thermal expansion is one of the factors at the root of this problem, and the question is would there be some advantage in having lower expansion coefficient alloys and is there a family of alloys based on some modifications of Invar which could prove useful.

COOLERS

Finally let us deal with coolers. The great majority of coolers are conventional tube exchangers with water on one side. The industry has learned how to design such exchangers to obtain reliable service using existing materials and working within existing properties. There are problems with specific designs, but it is quite easy to carry out this operation without calling for special properties from materials, and this is a subject hardly worth discussing. The more interesting aspect of the subject is that of expansion turbines. Clearly it is inefficient to degrade heat from 800-900° C down to steam-raising temperature such as 300° C as normally done, and it is attractive to consider expanders as a first step in the cooling system. This is done sometimes but it is not very popular because of reliability considerations. The potential savings which can be made would rapidly vanish if the expanders were to cause an unscheduled shut-down. Lack of corrosion and creep data in the specific environmetal conditions in the process streams in question is the uncertainty at present.

CONCLUSION

In order to summarise this paper, perhaps it may help by repeating the general message in a completely different way.

Lack of actual creep or rupture data is not the problem. As a rule this is the subject on which there is

most precision. Problems arise because we know far less about stress levels and because in practice actual temperature may be very different from calculated temperature. Each case trends to be a problem in itself, and it is a personal view that there is now more scope in attempting to solve each problem as a combined process design and materials problem rather than by doing general work on high temperature materials. Over the last three decades it has been worth doing generalised work, but a lot of the ground has been covered. The level of effort on this type of work may now be relatively too high, and it could be more profitable to divert some of it to actual specific problem-solving tasks.

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 163-171

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HIGH TEMPERATURE MATERIALS REQUIREMENTS OF THE METALLURGICAL INDUSTRIES

By

J. H. DAVIDSON

INTRODUCTION

There is a considerable overlap in the materials requirements of the metallurgical and other industries. Taking materials in the broader sense, there is one major field which concerns particularly, if not exclusively, the metallurgical industry, namely that of refractory ceramics; furnace and ladle linings etc. However, this subject being outside the author's range of competence, the discussion will be limited to metallic materials.

Some materials exposed to high temperatures are chosen chiefly for economic reasons; when time lost in replacement is insignificant, low life can be accepted on price grounds, for instance in the case of ingot moulds. It is proposed to consider here three areas of application in which, while the price factor remains important, materials properties limit process performance: hot-working tools, furnace parts, electric heating elements.

Generally speaking the principal requirements for high temperature materials are high mechanical strength and good oxidation/corrosion resistance. In the case of hot working tools, the most important factor is high temperature mechanical strength, whereas oxidation/corrosion resistance is the major prerequisite for electric heating elements and a combination of both is essential in materials for furnace parts.

HOT WORKING TOOLS

Materials for hot-working tools (forging anvils and dies, extrusion dies, hot shear blades, etc.). require high hot hardness, ability to withstand impact stresses and thermal shock and adequate abrasion resistance. The most commonly used materials are the hot-work tool steels with around 0.4 % C and various W, Cr, V, Mo or Co additions. These steels maintain a high resistance to deformation up to about 550 to 600° C. The important factors are the temperature of the tool, the time at temperature and the strength of the work material. Even in cases where tool steels give satisfactory performance, advantage can often be gained by using superalloy tools whose longer life offsets the increased cost. Figure 1 compares the hot tensile strength of tool steels and certain superalloys. The latter are employed for extrusion dies and for hot-working anvils and dies for forging superalloys, and this is the area in which progress is most likely to be situated.

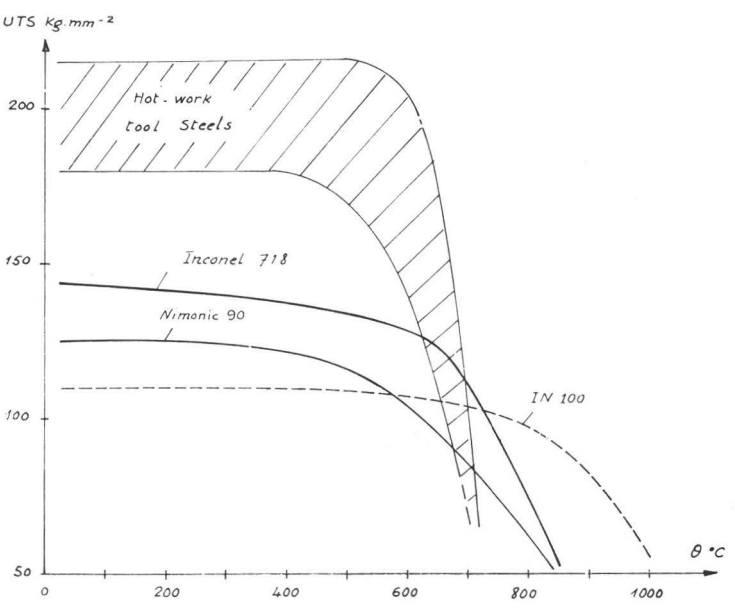

FIG. 1. — *Hot tensile strength of hot-work tool steels and of some nickel-base superalloys.*

The problem in hot-working superalloys is obviously that they have been designed to resist high temperature deformation. This resistance is derived from a combination of solid solution strengthening and precipitation hardening by intermetallics. Figure 2 shows that, to a first approximation, temperature capability increases with the total hardener content. As regards solution hardening, the most important aspect in creep is the reduction in diffusion rate.

This is greater the higher the melting point of the element added, and for the elements considered, the melting point increases with atomic weight. For this reason, the solid solution hardeners are plotted on a weight percent basis, whereas atom percentages are used for elements contributing to γ' precipitation hardening, since volume fraction is of major importance in this case. Niobium and hafnium are considered as solid solution hardeners in the diagram and ought

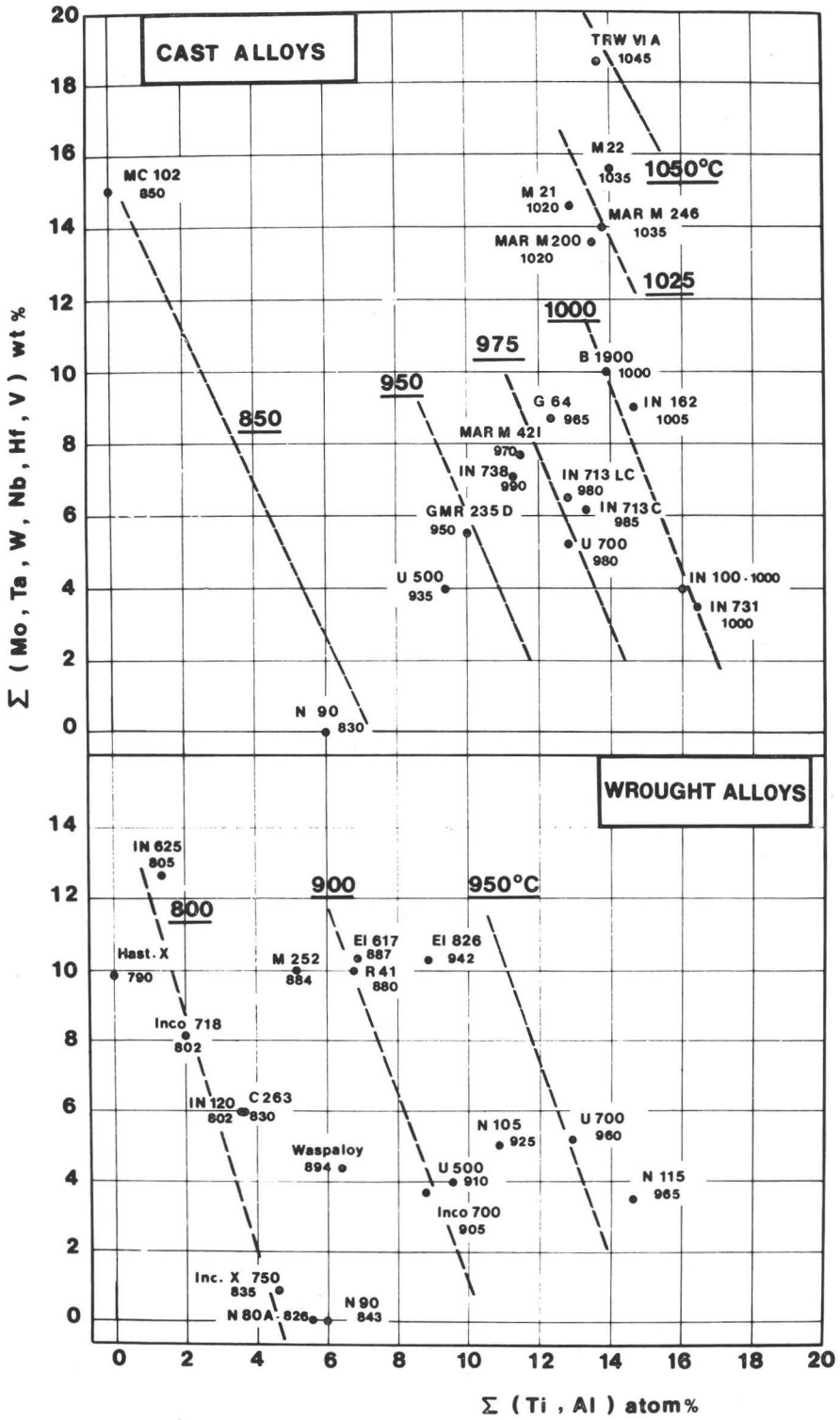

FIG. 2. — *Influence of composition on creep strength of nickel-base superalloys. Temperature for 100 hours rupture life at 14 kg. mm*$^{-2}$

perhaps more appropriately to be included as precipitation strengtheners, but in fact this produces little change in the overall result. Increasing volume fraction of intermetallic precipitates is accompanied by a continuous rise in solution temperature, figure 3, and leads to lower incipient melting temperatures and eventually to the formation of eutectic γ'. The relatively low flow stress region between complete γ' solution and the incipient melting temperature thus becomes progressively smaller. This is illustrated in figure 4 in which the behaviour of a purely solution hardened alloy (Hastelloy B) is included for comparison.

It would clearly be an advantage in the case of alloys with narrow single phase temperature regions to be able to maintain the work-piece temperature as long as possible. Furthermore, slow deformation rates lead

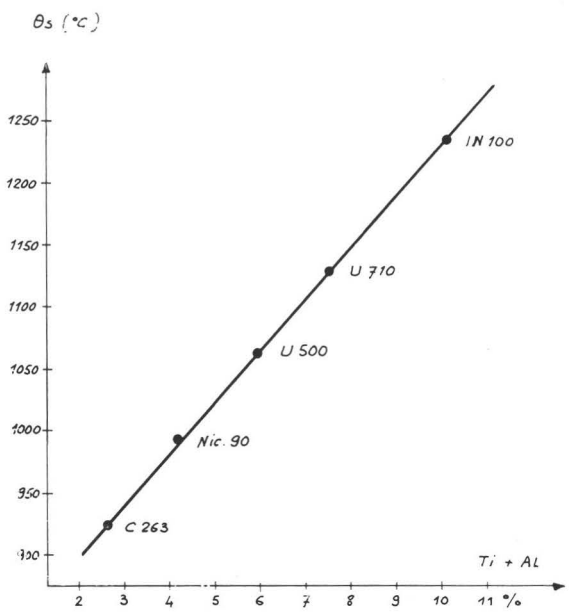

FIG. 3. — *Variation in γ'-solvus temperature with total* Ti + Al *content.*

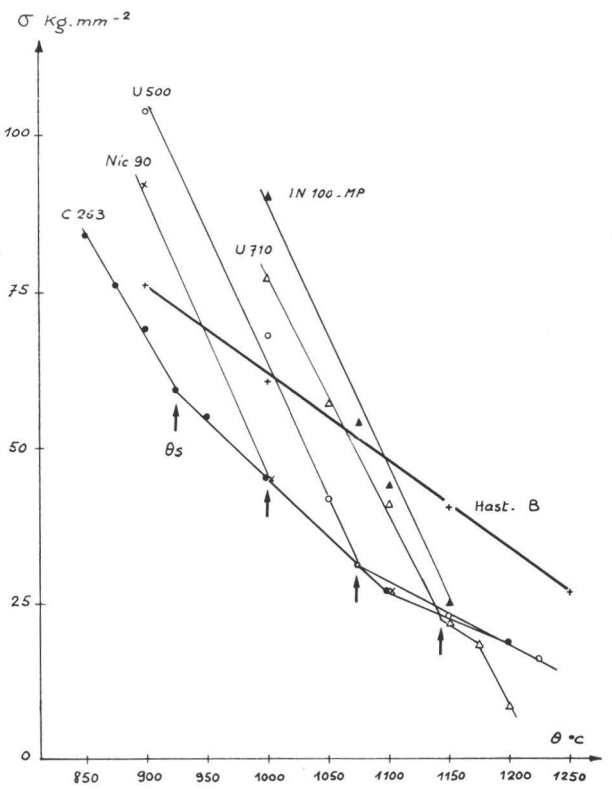

FIG. 4. — *Flow-stress vs. temperature curves determined by torsion testing. Strain rate 3.9 sec^{-1}.*

to lower flow stresses, figure 5, and even to superplasticity in the case of very fine-grained materials, such as can be obtained by powder-metallurgy techniques, at high temperatures. Similarly, slow strain rates lead to early recrystallisation, either dynamic (fig. 6) or static, with a consequent-increase in ductility (fig. 7).

It can be seen that isothermal or hot-die forging could open up considerable scope for the hot-working of superalloys and is particularly interesting now that powder metallurgy has made it possible to obtain for-

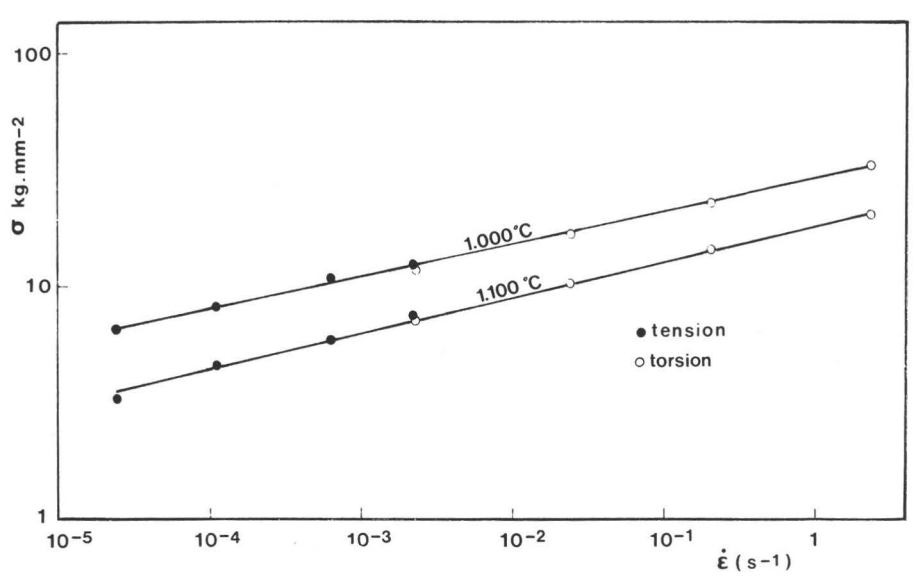

FIG. 5. — *Strain-rate dependence of flow-stress for the nickel-base superalloy C263. Data from tensile and torsion tests. Correlation using Von Mises criterion.*

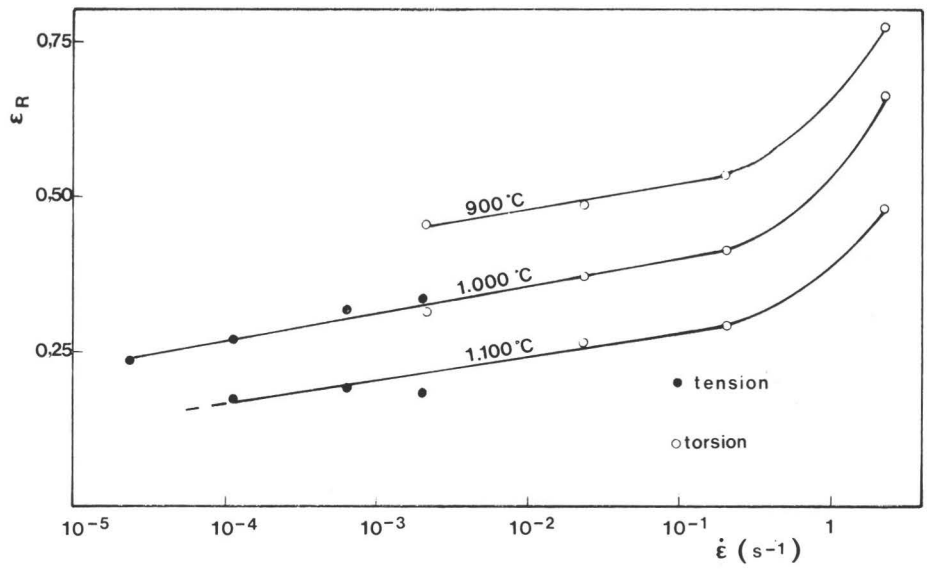

FIG. 6. — *Strain-rate dependence of strain to onset of dynamic recrystallisation in alloy C263. Data from tensile and torsion tests.*

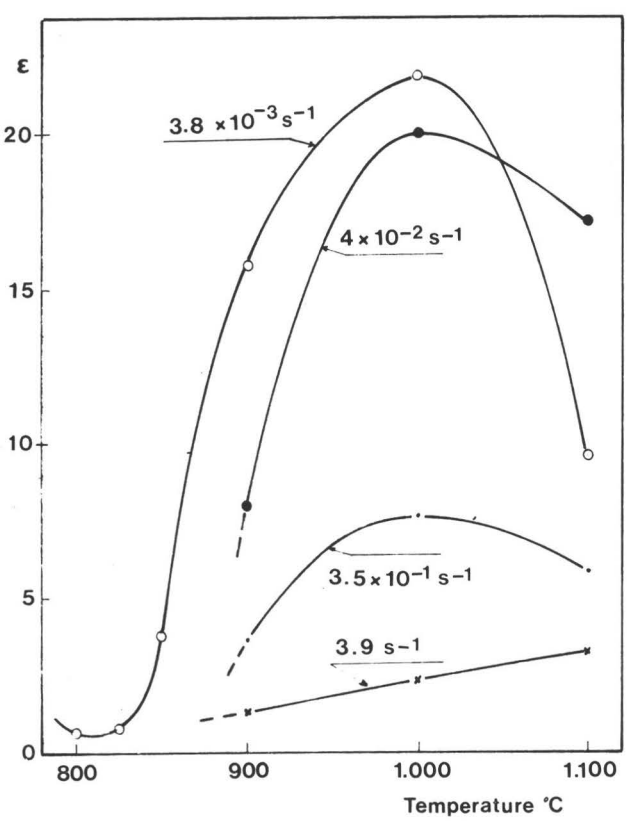

FIG. 7. — *Strain-rate dependence of ductility in torsion for alloy C263.*

geable alloys of higher strength. Apart from the need for special die-heating arrangements, the tool material presents the major obstacle. Molybdenum-based TZM alloy has been used for superplastic forming of powder metallurgy IN 100 [1], but as with other refractory alloys, oxidation resistance is extremely poor. Ceramic materials could probably be employed if care is taken to avoid excessive mechanical and thermal shock. Carbide and/or solution strengthened Ni or Co-base alloys with flatter flow-stress temperature curves might provide an answer, but little work seems to have been done in this field.

FURNACE PARTS

Furnace parts-muffles, rollers, rails, belts, baskets, etc. usually need both high temperature strength and oxidation/corrosion resistance to a greater or lesser degree depending on the application. Good thermal shock and wear resistance are also often required. The alloys used are generally solid-solution or carbide hardened. They are known as « heat-resisting » alloys and are capable of supporting lower stresses than the « superalloys », but can usually operate at higher temperatures.

Oxidation/corrosion resistance

Good oxidation resistance is obtained by the formation of a stable oxide film, impermeable to ionic diffusion. Most heat-resisting alloys owe their protection to a continuous surface film of Cr_2O_3, being based on the Fe — Ni — Cr system. Figure 8, plotted using the data reported by Brasunas *et al.* [2], shows the effect of composition on the oxidation resistance in this system. The optimum behaviour is obtained when the chromium content is sufficient for the formation of a continuous Cr_2O_3 layer. Less chromium is needed in alloys with higher nickel contents and the minimum rate of attack is lower. However, the results shown were obtained in short-time tests ($\sim$ 24 hours). In practice higher chromium levels are preferable, in order to replace losses due to spalling or evaporation in the form of CrO_3 or CrO_2.

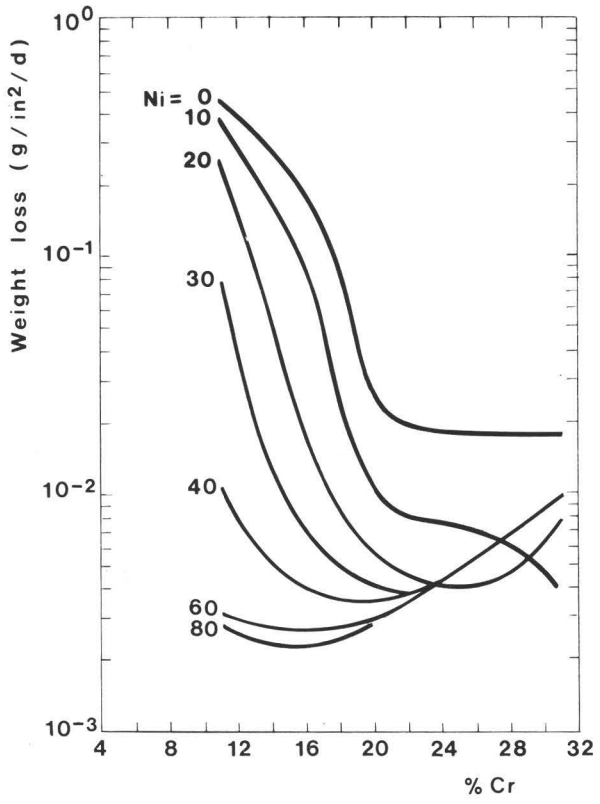

FIG. 8. — *Oxidation at 980° C of* Fe — Ni — Cr *alloys containing* ~ *0.4 % C and* ~ *1.2 %* Si. *Results taken from Brasunas* et al. [2].

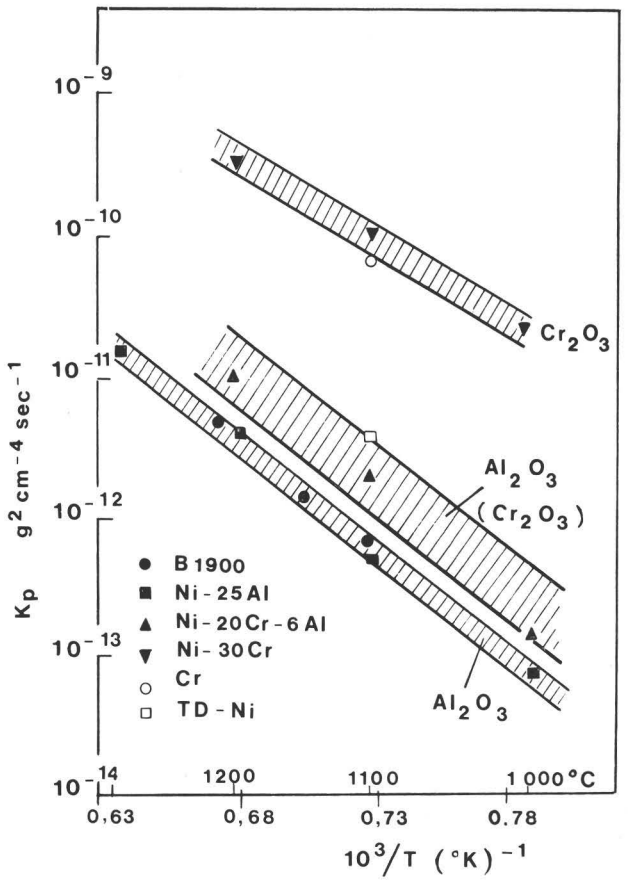

FIG. 9. — *Effect of oxide type on the oxidation kinetics of various alloys. After* Goward [3].

Al_2O_3 affords better protection than Cr_2O_3 as far as oxidation is concerned, due to a smaller concentration of ionic effects. This is illustrated in figure 9, after Goward [3]. Roughly 5 % by weight of aluminium is required to form a continuous film. However, apart from certain superalloys and Fe — Cr — Al heating element materials, which will be discussed in the next section, little use has been made of Al_2O_3 protection for furnace components.

Oxidation, and particularly spalling resistance, can be markedly improved by minor additions of « active » elements such as the rare-earths, but their use in commercial alloys is not yet widespread.

Although oxidation is the most common form of attack, corrosion by other species is often at least as important. In carburising atmospheres, an impermeable oxide is an advantage, since carbon penetration is limited. Nickel, which has little affinity for carbon and which improves thermal shock resistance due to higher ductility and lower thermal expansion, is generally favourable. However, the composition Ni-20 % Cr is especially vulnerable in strongly carburising conditions, since the ternary eutectic in the Ni — Cr — C system, which melts at 1,045° C, occurs at Ni-20 % Cr-3.5 % C. The liquidus temperature rises along the eutectic valley, reaching 1,305° C at 32 % Cr-2.2 % C [4]. In general, the chromium content should be sufficient to allow for losses due to carbide formation.

Because of its relatively high solid solubility and the slow kinetics of nitride formation, attack by nitrogen is not normally a problem, but can become more severe when it is present in the nascent state. In this case,

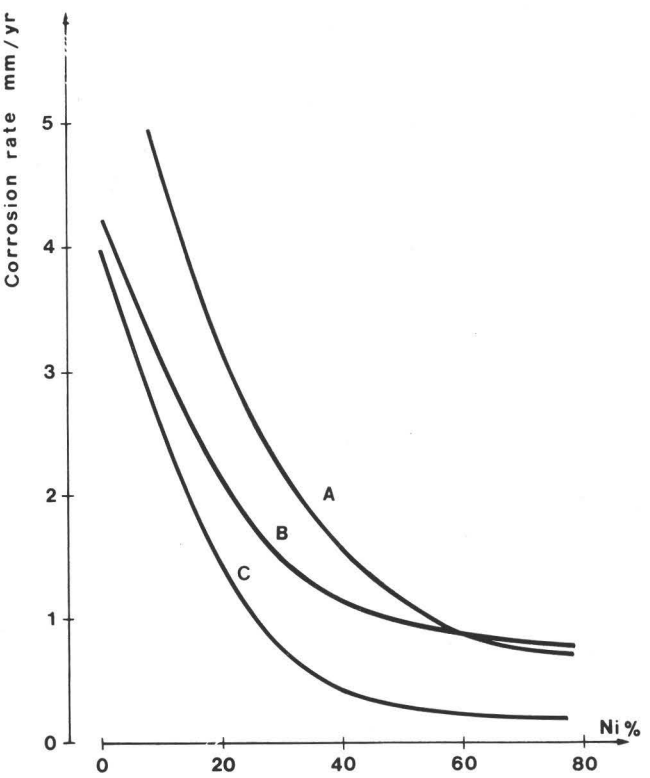

FIG. 10. — *Effect of* Ni *content on the corrosion rate of* Fe — Ni — Cr *alloys in three different nitriding atmospheres :* A. *586 hours in a nitriding furnace at* ~ *540° C,* B. *1 011 hours in an ammonia heater at 460° C,* C. *1 540 hours in an ammonia circuit at 500° C. After* Moran et al. [5].

as with carbon pickup, a high nickel content is preferable, as shown in figure 10, after Moran *et al.* [5].

Corrosion by sulphur-containing gases can be extremely deleterious, particularly under reducing conditions. This is due to the exceedingly low solid solubility of sulphur, together with the formation of low melting-point eutectics (645º C in the Ni — S system, 877º C for Co — S, 988º C for Fe — S and 1,350º C for the Cr — S system). Chromium, which forms a high melting-point stable sulphide is therefore a favourable element, whereas high nickel contents are deleterious. Sulfidation resistance can be considerably improved by fairly small additions of aluminium, as shown by Schultz *et al.* [6], figure 11.

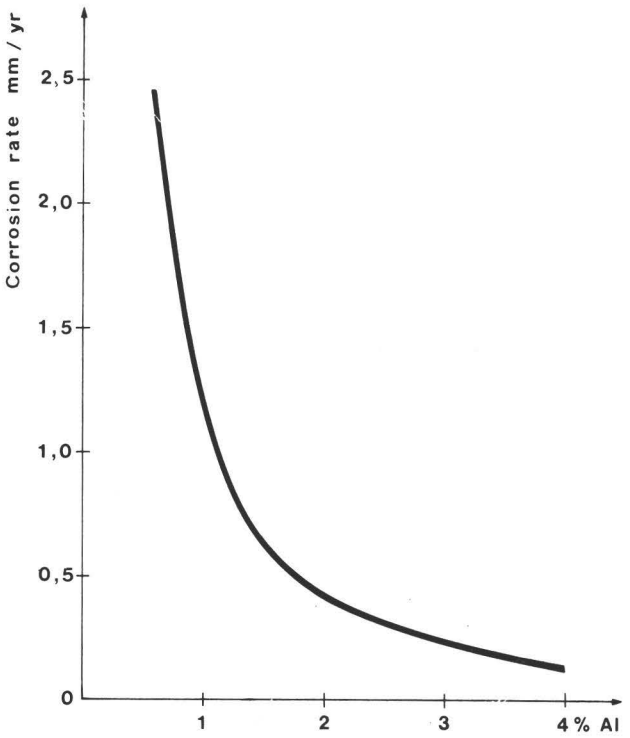

FIG. 11. — *Effect of aluminium on the resistance to sulphur attack of an alloy* Fe — 32Ni — 20 Cr *930 hours exposure at 593º C in an atmosphere containing 9 to 33 %* H_2S, *18 to 65 % light hydrocarbons and 2 to 72 % nitrogen. After Schultz* et al. [6].

In the case of corrosion by hot salts, of which the most severe are the halides, the main requirement for satisfactory resistance is a high chromium content, as has also been found for the combined attack by sulphur and NaCl, frequently encountered in marine turbines [7, 8], and the same is true for resistance to vanadium containing ashes.

Creep resistance

The mechanical strength required of furnace parts is in general fairly moderate, in many cases being limited to the ability of the component to support its own weight.

Figure 12 shows the location of some of the most commonly used matrices in the Fe — Ni — Cr system.

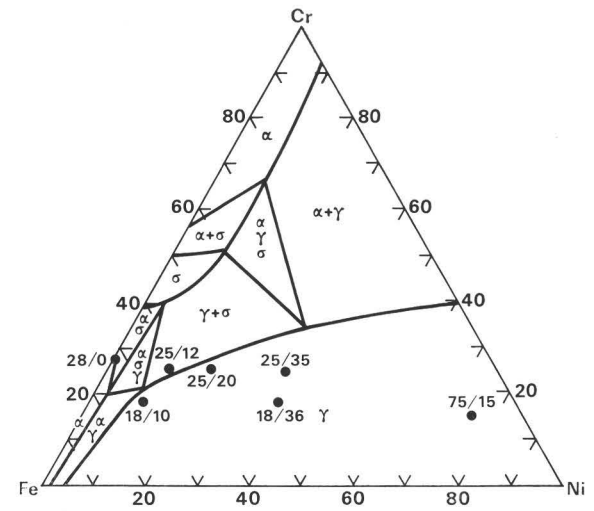

FIG. 12. — *Some common heat-resisting alloy matrices based on the* Fe — Ni — Cr *system (650º C section. Metals Handbook 1948).*

At medium temperatures, low stacking fault energy (compositions near the austenite phase boundary) is probably important for good creep strength, whereas high nickel content (low diffusivity) seems to be more important at higher temperatures, figure 13.

Considerable hardening is obtained by carbon additions, figure 14, and many heat resisting alloys produced as castings contain about 0.4 % C. Solid solution hardening is often enhanced by alloying with elements such as tungsten, molybdenum and niobium. Cobalt probably strengthens mainly by lowering the stacking fault energy. Total additions are limited by sigma

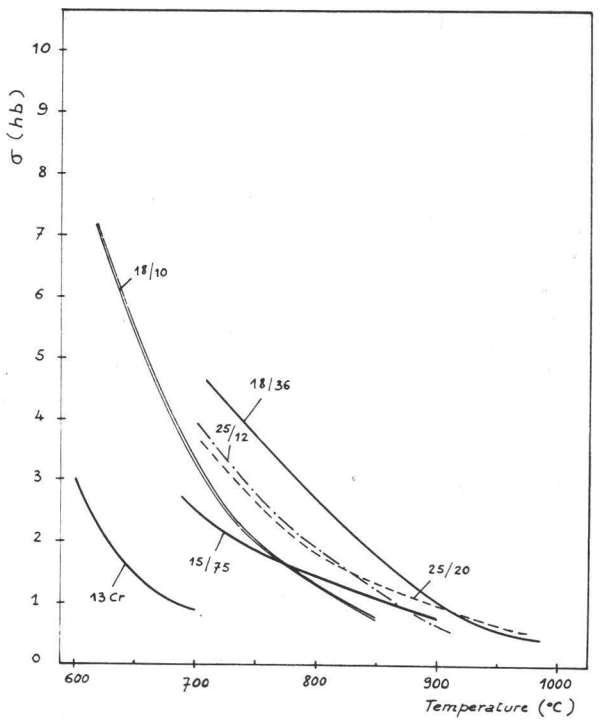

FIG. 13. — *Creep strength of some simple heat-resisting alloy matrices. Stress for 1 % elongation in 10,000 hours. Figures indicate* Cr *and* Ni *contents, balance* Fe.

phase formation. They can be higher in more nickel-rich matrices, but the price factor is often the major obstacle. Figure 15 shows the effect of various additions to an Fe — 35Ni — 25Cr matrix, while figure 16 compares these same materials with a number of more special commercial alloys, whose nominal compositions are

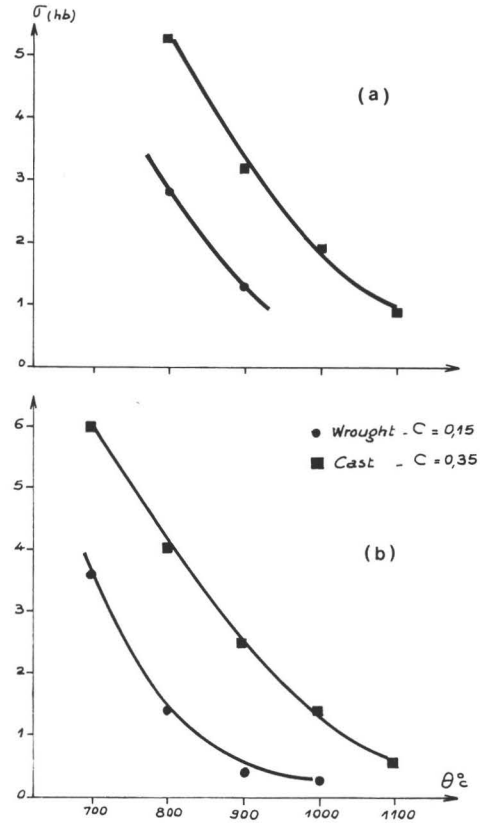

FIG. 14. — *Effect of carbon content on the creep strength of a 25 % Cr — 20 % Ni steel;* (a) *stress for rupture in 1,000 hours;* (b) *stress for 1 % elongation in 10,000 hours.*

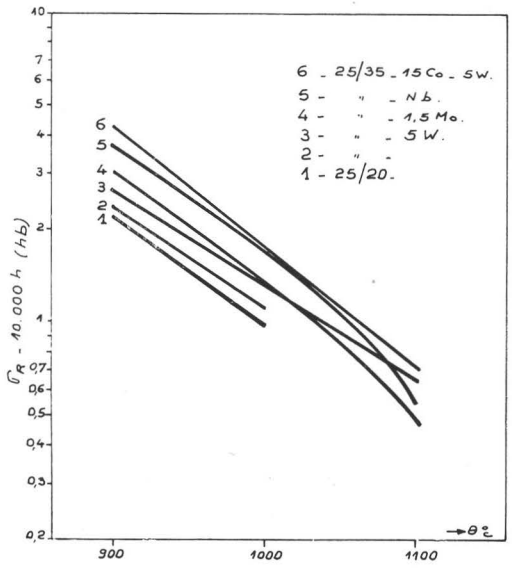

FIG. 15. — *Effect of various alloying additions on the creep strength of cast* Fe — Ni — Cr *heat-resisting alloys containing 0.4 % C.*

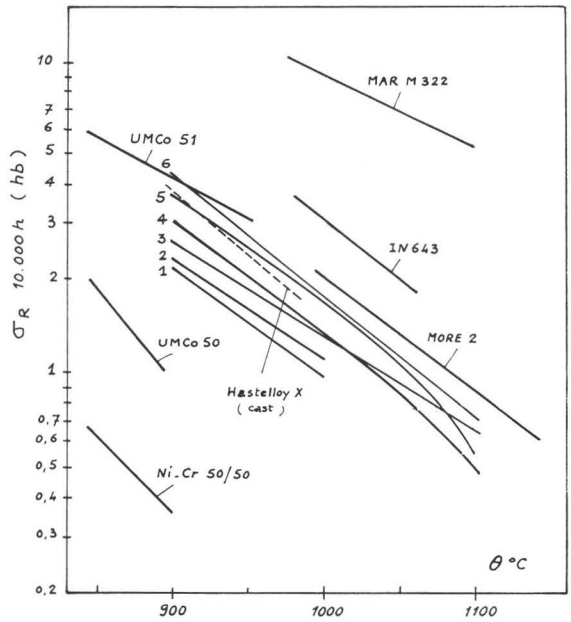

FIG. 16. — *Comparative creep strength of certain commercial heat-resisting alloys.*

given in table I. Among these, the cobalt-base superalloy MAR M 322 represents the upper performance limit of its category. The poor creep resistance of the Ni — 50Cr composition, developed for use in conditions of severe vanadium corrosion, has been greatly improved by an addition of 1.5 % Nb in the alloy designated IN 657, whose creep strength is comparable to that of a 25 % Cr-20 % Ni steel (curve 1 in fig. 16). The UMCo-50 and UMCo-51 grades, the latter of which contains 2 % Nb in the Fe — 50Co — 28Cr matrix, are extremely insensitive to attack by slags and molten salts and have excellent wear and thermal shock resistance. The alloy IN 643 is an alloy developed for the manufacture of cast tubes for the petrochemical industry, and is a good illustration of the problem which faces the alloy-designer in this field, namely that of obtaining a maximum combination of creep strength and corrosion resistance while avoiding the formation of embrittling sigma phase.

ELECTRIC HEATING ELEMENTS

Electric heating elements can be considered as a special type of furnace component. Except in the case of the ferritic Fe — Cr — Al alloys, the main problem is that of oxidation/corrosion resistance, but there are also certain physical property requirements: high electrical resistivity, low temperature coefficient of resistivity and high thermal emissivity of the oxide layer. The mechanical strength level needed is low; an element must be able to support its own weight and must be sufficiently ductile to absorb thermal strains. However, this aspect becomes important if resistance to environmental degradation makes it possible to work at very high homologous temperatures.

TABLE I. — *Nominal compositions of alloys figuring in the text (wt %).*

Alloy	C	Fe	Ni	Co	Cr	W	Mo	Mn	Ti	Al	Mn	Si	Zr	Ta	V
T 63W, Mo-RE 1.	0.4	bal	33	—	25	5	—	—	—	—	1.0	1.5	—	—	—
Manaurite 35 D.	0.45	bal	35	—	25	—	2	—	—	—	1.2	1.2	—	—	—
Manaurite 36 X.	0.4	bal	33	—	25	—	—	1	—	—	1.0	1.5	—	—	—
Supertherm . .	0.4	bal	35	15	25	5	—	—	—	—	1.0	1.5	—	—	—
MO-RE 2. . .	0.4	—	bal	—	33	17	—	—	—	—	—	—	—	—	—
IN 643. . . .	0.5	3	bal	12	25	9	0.5	2	0.15	—	< 0.3	< 0.3	0.08	—	—
Hastelloy X . .	0.1	18.5	bal	1.5	22	0.6	9	—	—	—	⩽ 1	⩽ 1	—	—	—
IN 657. . . .	0.1	⩽ 1	bal	—	50	—	—	1.5	—	0.15	—	—	—	—	—
Umco-50 . . .	0.08	bal	—	50	28	—	—	—	—	—	0.8	0.8	—	—	—
Umco-51 . . .	0.35	bal	—	50	28	—	—	2.1	—	—	0.8	0.8	—	—	—
Mar M 322 . .	1.0	—	—	bal	21.5	9	—	—	0.75	—	—	—	2.25	4.5	—
Nimonic 90 . .	0.07	—	bal	19	19	—	—	—	2.50	1.50	—	—	—	—	—
C 263	0.06	—	bal	20	20	—	5.9	—	2.15	0.45	—	—	—	—	—
U 500	0.10	—	bal	18	18	—	4.0	—	3.0	3.0	—	—	—	—	—
U 710	0.07	—	bal	15	18	1.5	3.0	—	5.0	2.5	—	—	—	—	—
IN 100 . . .	0.18	—	bal	15	10	—	3.0	—	4.7	5.5	—	—	—	—	1.0

Except in cases of forced convection, the heat, W, lost from an element is almost exclusively due to radiation, so that

$$W = \varepsilon\sigma S(T_E - T_F)^4$$

where ε is total emissivity, σ is Stefan's constant, S is the total radiating surface area, T_E is the temperature at the element surface and T_F is the furnace temperature. This heat is produced by the current in the heater elements, and is also given by

$$W = \frac{V^2A}{J\rho L}$$

where V is the applied voltage, J is the mechanical equivalent of heat, ρ is the resistivity, A is the cross-sectional area of the elements and L their total length.

Because dimensions are limited by a need for a compromise between mechanical strength and environmental resistance on the one hand and radiating-surface-to-volume ratio on the other hand, and since convenient operation demands reasonable current and voltage levels, this places requirements on the resistivity. Thus, in practice, values ranging from $\sim 10^{-5}$ to $\sim 50\ \Omega.cm$ are acceptable, although $10^{-4}\ \Omega.cm$ is a more usual lower limit.

While more exotic metallic materials can be used in some special small-scale furnaces, and although certain refractory compounds are beginning to find industrial applications at very high temperatures, by far the major part of all heating elements are made from alloys based on the Fe — Ni — Cr and Fe — Cr — Al systems, and the present discussion will be limited to this range of products.

Approximate isoresistivity contours are plotted in figure 17 for the Fe — Ni — Cr system and in figure 18 for the Fe — Cr — Al system. The beneficial effects of chromium and aluminium, and of nickel in iron-rich alloys, are clearly visible.

Since a resistivity of about 80 to 100 $\times\ 10^{-6}\ \Omega.cm$ is generally considered to be a minimum value for convenient operation, the principal alloys in the Fe — Ni — Cr system are austenitic. Because of this, creep strength is not usually a problem, life being limited chiefly by oxidation-corrosion. As has been discussed in the section dealing with materials for furnace parts, good

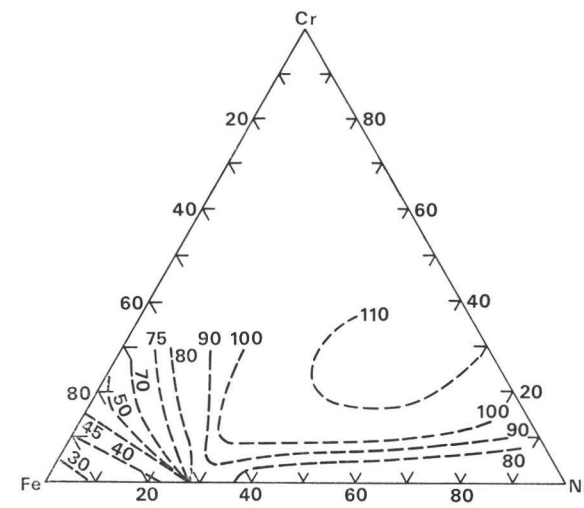

FIG. 17. — *Iso-resistivity contours in the* Fe — Ni — Cr *system* ($\mu\Omega.cm$ *at 20° C*).

environmental resistance requires at least 15 % Cr and, except in the case of sulphur-containing atmospheres, performance improves with increasing nickel content. Many of these alloys also contain 1 to 2 % Si and this increases both oxidation resistance and electrical resistivity.

Alloys based on the Fe — Cr — Al system, with 20 to 30 % Cr and 4 to 6 % Al, whose electrical resistivity is high and varies little with temperature, offer exceptional oxidation-corrosion resistance at elevated temperatures, due principally to the formation of a continuous Al_2O_3 surface film. Furthermore, the solidus temperature is in the region of 1,500° C, compared with values between 1,355 and 1,410° C for the austenitic Ni — Cr and Fe — Ni — Cr grades. However, the ferritic structure leads to mechanical property limitations, namely low creep strength and lack of ductility. The ductile to brittle transition characteristic of body-centered cubic materials occurs at around 100 to 200° C in these alloys, so that it is advisable to carry out final forming operations between 200 and 300° C for thick sections. Rapid grain-growth, which sets in above about 850 to 900° C, enhances the embrittlement,

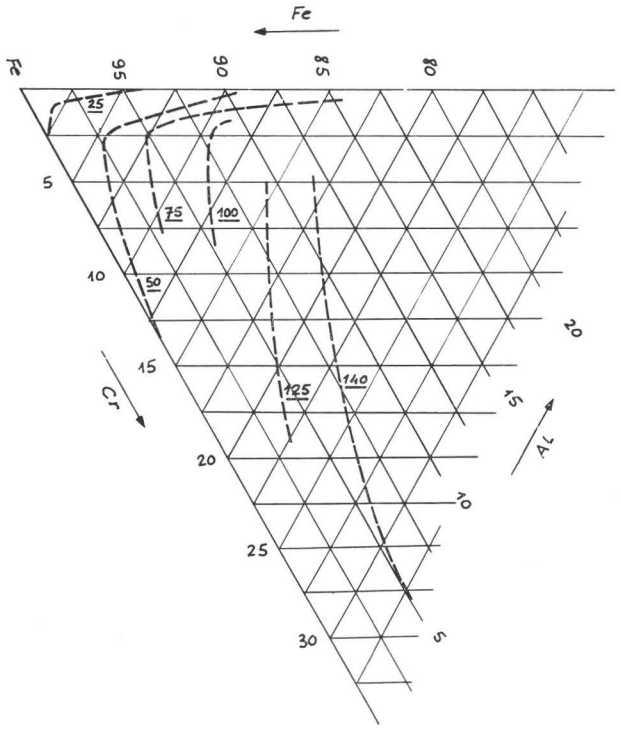

FIG. 18. — *Iso-resistivity contours in the* Fe — Cr — Al *system* ($\mu\Omega.cm$ *at* 20° *C*).

leading to an almost glass-like behaviour at room-temperature after service in this range. Ductility can also be decreased by the phenomenon known as « 475° C embrittlement » which occurs on exposure at temperatures between 400 and 550° C, and which is generally attributed to either an order-disorder reaction or to a very fine precipitation. However, this temperature region can usually be largely avoided in practice and the embrittling reaction is reversible, the initial condition being restored by annealing for a few minutes at 600° C. While the lack of ductility makes the Fe — Cr — Al alloys difficult to manufacture and delicate to use, the most common cause of failure at high temperatures is excessive creep deformation, entraining local thinning or short-circuiting. In spite of these drawbacks, the ferritic alloys are widely used since they represent the highest temperature capability of the common metallic materials and because of their relatively low price.

Future trends will probably see more generalised use of rare-earth additions for increased oxidation/corrosion resistance. However, the ferritic alloys have by far the best inherent temperature capability, due to their high melting points, and would be assured of more widespread use if the problems of creep strength and embrittlement could be solved.

CONCLUSIONS

Three fields of particular interest to the metallurgical industries have been described, in which materials requirements are especially demanding. While at the forefront of technological advance appreciable further progress in performance will probably require the introduction of ceramics, in the majority of cases cost is a primordial factor, and much can still be done to improve the price: service-life ratio in metallic alloys. This paper, which has only treated metallic metarials, has attempted to outline the present situation and to point out areas in which improvement is desirable, without necessarily pretending to provide the answers.

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DEVELOPMENT OF MATERIALS USED IN GAS TURBINE ENGINES. R AND D GUIDE LINES AND PROPOSALS FOR A PRIORITY SCHEME (*)

By

P. ESSLINGER and H. HUFF

1. *INTRODUCTION*

This paper intends to give guide lines for the materials development of gas turbine engines used in aircrafts. Furthermore, our own efforts at MTU to produce a priority scheme for these subjects will be shown.

2. DRAWING UP A LIST OF SUBJECTS

2.1. Groups of subjects

The product will always determine the development of materials in an industrial enterprise. In addition, in a mechanical-engineering enterprise, the expression « Development of Materials » is generally given an interpretation different from that given in the supplier industry.

It is not taken to mean the development of new alloys of versions of alloys. These are assumed (at least laboratory-wise) to be familiar. Materials development can be defined as:

a) the development of functioning components from (new) materials;

b) the determination of material behaviour, with a view to components, constituting the basis for a dependable design;

c) the quantitative determination of the effect of material defects on service life and, finally;

d) the securing of uniform quality.

This general orientation of the development of materials in the mechanical-engineering industry is based on the recognition, that manufacture, configuration and (material) properties are nearly always interrelated, most pronouncedly in the case of parts made from composite materials.

In the mechanical-engineering industry, the development of materials is, therefore, in the ultimate analysis a service for Engineering, Stress Analysis, Manufacturing and Quality Control. With regard to the product, an expedient distinction can be made between various spheres of requirements for this work, because there are characteristic differences in the approach, definition of the subject, implementation and yardstick for rating.

In the language of engine manufacturing, these are:

— the (component-wise) preparations for the development of future engines (project-stage);

— making available of data on materials and making available of components for engines being currently developed (drawing-board and development stage);

— improvement of engines and making them less expensive in the prototype or production stage;

— other requirements (*e. g.* rationalization, ecological impact).

(*) Previously published (in German) in *Zeitschrift für Werkstofftechnik*, 1976, *5*.

In line with these four spheres of requirements, groups of subjects for tasks in the development of materials shall now be discussed.

2.2. Subject Group 1: Preparations for the development of future engines

In engine manufacture, future development can be summed up under four slogans: *hotter*, *lighter*, *more reliable*, *less expensive*.

This sequence indicates no priority. Many factors will determine the actual sequence, such as: whether engines for airborne or land-bound vehicles, for civil or military applications are involved.

However, the conceivable engineering solutions to problems can be set down, irrespective of this.

Figure 1 characterises roughly the progress over the past twenty years, comparing typical performance figures for present day military engines with those of about twenty years ago. Over this period, the thrust/weight ratio has been stepped up some 40 %, mainly as a result of:

— significant progress in process engineering, especially in welding technique and in investment casting;

— the extended use of titanium in compressors;

— the development of new high temperature materials, *e. g.* IN 100 for blading, Waspaloy and Inco 718 for discs. These are compared with former materials in figure 2.

These new technologies have made an advanced design possible, admittedly, a correspondingly higher price having to be taken into consideration.

In this context, the following item is of interest: turbine inlet temperatures have risen about 400° C over the past twenty years, while the temperature which the material of the turbine blades can reasonably be expected to withstand has risen only some 70° C. It follows that about only one-fifth of the rise in the gas temperature—so important for the efficiency—can be looked at as a success in the development of alloys. The remaining 80 % can be seen to be progress in investment casting hand-in-hand with engineering developments. These have led from the uncooled solid blade via internally cooled hollow blades to the blade with additional film cooling, complex gas routing in the interior (extra-impingement cooling) and electrochemically drilled minute cooling holes near the leading and trailing edges.

Jahr des Erstfluges	Leistungsmerkmale: Turbinen-eintritts-temperatur °K	Leistungsmerkmale: Turbinen-schaufel-temperatur °K	Leistungsmerkmale: Schub[1]/Gewicht	Aufwandsmerkmale: Preis/Schub[1] DM/N	Aufwandsmerkmale: Preis/Gewicht DM/N
1955	ca. 1200	ca. 1200	ca. 2,5	ca. 20	ca. 50
1975	ca. 1600	ca. 1270	ca. 3,5	ca. 60	ca. 200
Differenz absolut	400	70	1,0	40	150
prozentual	33 %	6 %	40 %	200 %	300 %

[1] Standschub bei Kampfleistung

FIG. 1. — *Increase of jet-engine performance in military aircraft.*

Anwendung	Werkstoff: Gebrauchsbezeichnung	C	Cr	Co	Mo	Ti	Al	B	Zr	V	Fe	Ni	Nb	Leistungsmerkmale: Relative Einsatztemp. °C[1]	Leistungsmerkmale: $G_{0,1/100^h}$ bei 600 °C N/mm²
Turbinen-Schaufeln	Udimet 500	0,08	19	18	4	2,9	2,9	0,005	-	-	4[2]	Rest	-	ca. 850	-
	IN 100	0,18	10	15	3	4,7	5,5	0,014	0,06	1	1[2]	Rest	-	ca. 950	-
Turbinen-Scheiben	A 286	0,05	15	-	1,25	2,15	0,2	0,003	-	0,3	Rest	26	-	-	450
	Waspaloy	0,06	19,5	13,5	4,3	3	1,4	0,006	0,05	-	2[2]	Rest	-	-	700
	Inco 718	0,04	19	-	3,1	0,9	0,4	0,006	-	-	18,5	Rest	5	-	720

[1] Definiert als diejenige Temperatur, wo $G_{0,2,100^h/T} = 2$ km ist.

[2] Maximalwerte

FIG. 2. — *Comparison of the performance of some high-temperature alloys.*

The next goal will be the effusion-cooled blade. Figure 3 demonstrates this progress in cooling-technique. It can almost certainly be predicted that the important parameters—gas temperature and thrust/weight ratio—will not undergo such a stormy development in the future as in the past twenty years. Successes will be smaller at a greater price, not only because scarcely surmountable barriers are increasingly being encountered, but also because the serious question of the purpose of ever more progress in performance, regardless of the cost involved, is posed. Work on bringing down the cost of engines and increasing the safe life between overhauls is, therefore, likely to figure more prominently in the foreground in the future.

Figure 4 is an attempt to allocate conceivable problem solutions to the future requirements on the product, higher gas temperature (*i. e.* efficiency), higher thrust/weight ratio for the same or improved reliability and the same or lower price.

Specific general subjects areas (centre column) from which problem solutions can be expected can be allocated in each case to the general goals (left-hand column), arrows being used to show the interrelationships.

In the right-hand column, topics from which we are, in principle, expecting progress towards the general goals are allocated to the subject areas, their study being considered generally desirable. This says nothing about the priority accorded to the particular topic. As will be seen later it may be very low.

Naturally, each topic must be considered to constitute the sum of various detailed tasks, these tasks being quite specifically oriented towards particular types of engine. On this point, going into greater detail

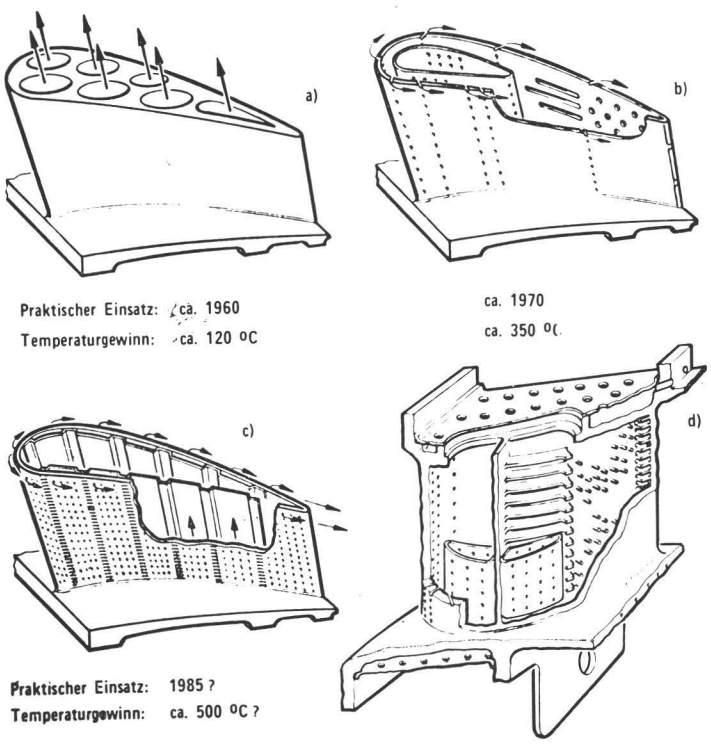

FIG. 3. — *Development of the cooling technology of turbine blades.*

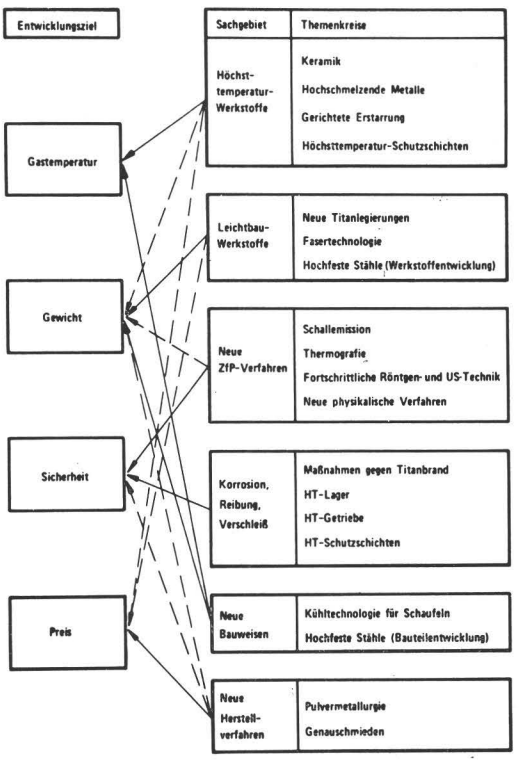

FIG. 4. — *Future orientation of material development.*

can be dispensed with. On the other hand, explanations seem called for in the case of some items of figure 4.

It may seem surprising that the subject « High-temperature materials » is also expected to have a positive effect on weight and price. This expectation relates solely to the topic « ceramics ». If, in fact, certain hot parts for turbines, nowadays being made from expensive metallic materials, could successfully be replaced by ceramic components, these parts could then really become less expensive and have less weight.

The topic « Protective Coatings » in this area is to be viewed solely in connection with high-melting-point metals, in particular niobium. The use of niobium alloys in engines can be considered seriously only if protective coatings, which function absolutely reliably in the face of hot-gas corrosion have been developed beforehand.

On the subject of « light-weight materials », a price advantage can be expected from « Fibre technology » if, for instance, the development of gearbox parts (mainly gearbox casings) from carbon-fibre-reinforced plastics can be realised. Moreover, this seems to be the most promising medium-term field of application to us for fibre-reinforced materials for engines, whereas still unsolved engineering problems stand in the way of their use for rotors.

In our opinion the development of new nondestructive testing methods grows in importance in step with the utilization of present-day materials, up to the limits of their loading capacity in the interests of a high thrust/weight ratio, which is a growing tendency. We came across a symptomatic example of this:

Figure 5 shows the fracture surface of a blade which broke at the root after a running time of 200 hours.

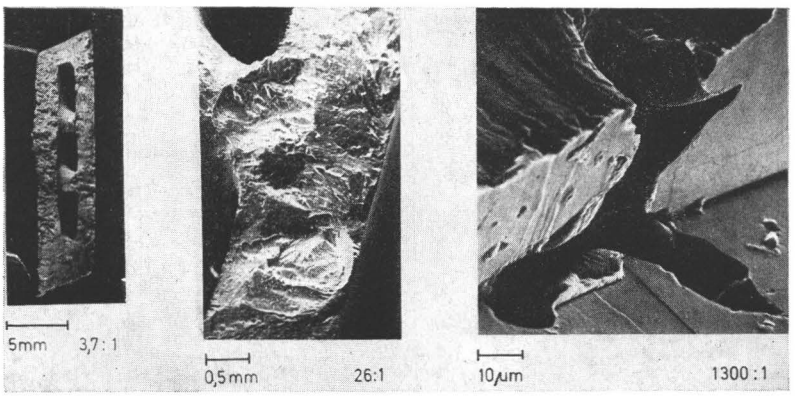

FIG. 5. — *Fracture surface of a turbine blade.*

The origin (but not the sole cause) of the fracture was a visible local pore which was acceptable according to the materials specification, simply because there is, at present, no nondestructive-testing method which enables pores of this small size to be detected: as such porosity is then inevitable with the present state of testing technology, allowance must be made for the scatter in fatigue strength by fixing minimum figures and safety factors accordingly, at the expense of weight. Such pores, which are not detectable at present, could be confined to lightly stressed zones, at least if testing technology were improved. This would limit scatter more and make better utilization of the materials possible.

This example should make it clear why we think the development of new nondestructive-testing methods will have a advantageous effect on engine weight.

There is also a perceptible lack of nondestructive-testing methods for making a reliable assessment of the quality of electron-beam and inertia welds, as well as of composite materials.

The « Protective Coatings » mentioned under the subject « Corrosion, Friction and Wear » are to be understood as further development or new development of the conventional protective diffusion coatings for turbine blading. This may cause surprise, as such protective coatings have been used for years—apparently without serious difficulties—and the technology must be assumed to be familiar. Whereas the two latter statements are largely correct, the usefulness of these coatings is nowadays a subject for discussion. Work in our own laboratory has shown, that coatings of the present state may have a negative influence on creep strength of blades.

On the other hand, the effect such coatings have in restricting oxidation for several thousand hours cannot be questioned. The development goal is thus clearly outlined: coatings just as good as the present ones in preventing oxidation but which do not reduce the initial mechanical strength.

The cooling-technology topic listed under « New Methods of Construction » is a logical follow-up to the remarks made on figure 3. The goal which must be evoked is the effusion cooled turbine blade. This type of blade is expected to produce higher gains in gas temperature than any new material, with the possible exception of ceramics.

The listing of « high-tensile steels » likewise under this subject is based on the following consideration: were the compressor discs, nowadays being made from titanium, to be made from maraging steels, the same design being used and the high specific strength being fully exploited, the rigidity as a function of the fourth power of the wall thickness would be inadequate. The consequent logical choice for the drum-type method of construction involves no improvement in weight. The goal for development must be a compromise worked out by Materials Technology and Engineering between these two extremes. Figure 6 is an attempt to illustrate this schematically.

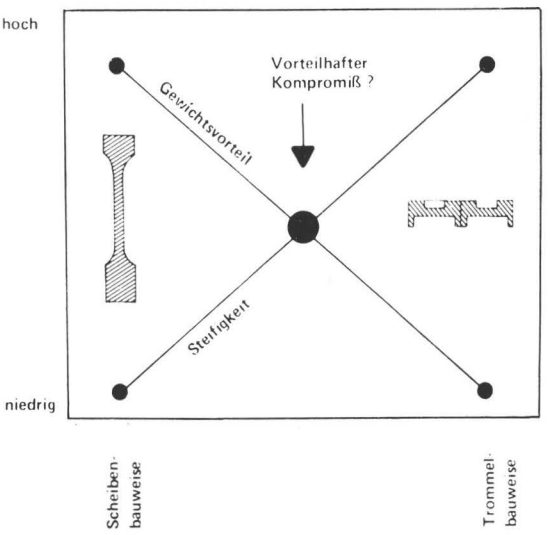

FIG. 6. — *Compromise for rotors of maraging steel.*

« Powder Metallurgy » and « Precision Forging » listed under « New Manufacturing Processes » revolve primarily around the following problem: owing to the dictates of forging, testing and quality assurance, the weight of ingots for titanium and other disc materials is far above that of the finished parts produced from them. The excess volume (up to 90 % in the case of titanium) has to be machined away, this being not

only an unacceptable waste of material in the long run but also the cause of high costs.

The idea of eliminating this cost-consuming material waste by close-to-contour hot isostatic pressing (in one operation) or by precision-forging should, therefore, be considered.

The use of powder metallurgy in combination with thermo-mechanical processing (« gattorizing ») most probably entails not only commercial but also engineering advantages: isotropy, homogeneity and less scatter in the properties even of large parts; greater ductility; in the case of nickel, greater high-temperature strength (fig. 7) and the possibility of using highly creep-resistant blade-materials also for discs; in the case of titanium, the elimination of coarse grains, harmful segregations and internal stresses and therefore better safeguards against life-endangering, premature and unexpected failures of compressor discs.

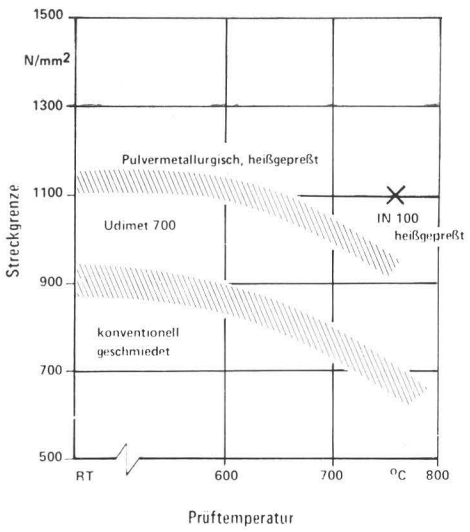

FIG. 7. — *Strength advantage of power metallurgy discs.*

In general, the development topics of subject group 1 reviewed here can be considered longterm programmes, the results of which will scarcely be utilised in engines now already in the development or prototype stage.

2.3. Subject Group 2: Making available data and components for engines being currently developed

In this case, short to medium term programmes are involved for engines which are in the development phase (starting with the design phase). In programmes of this category, the following indispensible prerequisites for the development of an engine are met:

— making available data on materials for the design of engine components;

— development of a satisfactory, reproducible component standard (usually in conjunction with suppliers);

— determination of the operational behaviour of defective components, as a basis for concessions;

— elimination of weak spots recognised at an early stage and of serious manufacturing difficulties.

As the design of an engine has already been fixed in principle in this phase, any work aimed at such a goal—for example a marked increase in gas temperature—could be too late in any case. In this phase, higher gas temperature is therefore not a priority goal. On the other hand, a limited reduction in weight can certainly be considered, particularly if the early engine trials do not yield the expected thrust/weight ratio. However, primary goals are the making available of data on materials and the working-out, materials-wise, of a reliable standard of components for the planned service life.

Analogous to figure 4, figure 8 sets down the interrelationship of goals, subject areas and conceivable topics for this type of development work. The topics given are doubtlessly not as spectacular as those in the previous group, but the results of work on them are absolutely necessary for the development of an engine. It can be taken for granted, that any advances in engine building, which are based on advances in materials, could not be put into practice without work of this sort. Implementing a new idea is just as intelligent as the idea itself: engineering progress is possible only if inspiration is in a balanced proportion to perspiration.

A few remarks on the topics are required for a better understanding:

The designation « Materials Mechanics » embraces work serving to calculate quantitatively, as accurately as possible from simply derivable characteristic data, the minimum service life of components which are subject to complicated mechanical stressing. Special importance is attached to the transferability to components of results obtained from test specimens, as well as to the effects of defects in materials. Two examples are given to illustrate these points: Apart from extensive cut up tests, test-bed and other engine running is necessary in order to approve a new disc material, a new design of a disc or even just a new supplier. Altogether, the new certification of discs swallows up funds to the order of one million deutschmarks.

There is, therefore, a need for work which enables us, to certificate discs and new disc materials mainly by cheap test sample work in conjunction with a calculation process. An example of a partial result of this type is given in figure 9. In the study underlying this graph, LCF strengths of plain and notched test specimens in INCO 718 (disc material) under controlled strain are compared with readings taken on discs at cyclic spin tests, using a method of calculation developed by Neuber.

As can be seen, there really seems to be a monotonic relationship between the life calculated from the specimens and that observed in the cyclic spin test. Meanwhile, we realise that we cannot in all cases be so lucky.

The second example concerns the mechanics of welded materials, at the point where they are welded together. The two, presently, most important materials for turbine discs, Waspaloy and Inco 718, cannot be welded free from cracks even with the electron beam.

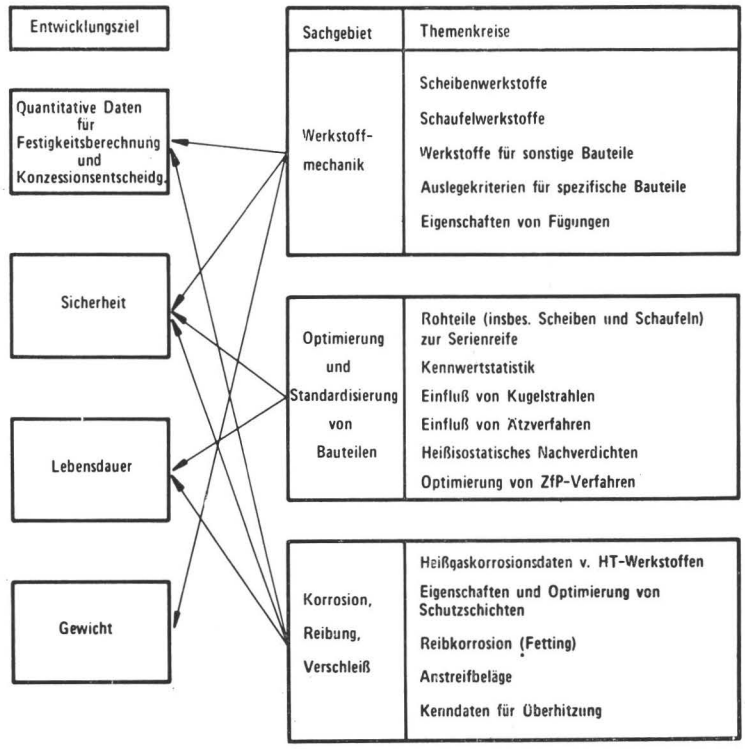

FIG. 8. — *R and D in material technology for turbine-engine development.*

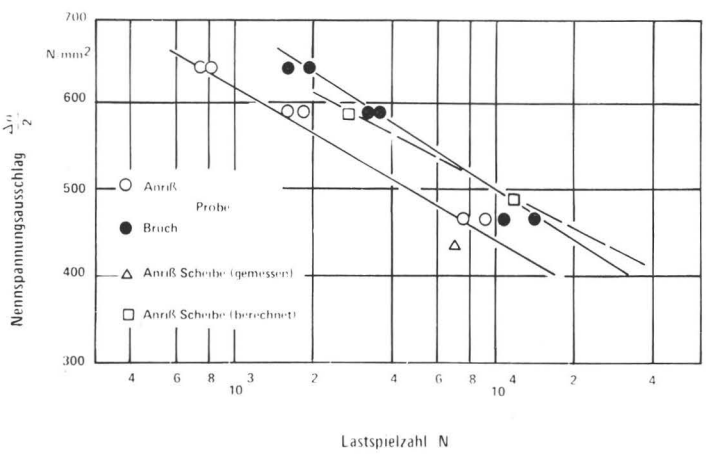

FIG. 9. — *Low-cycle fatigue strength of Inco 718 discs.*

At the present state of the materials and welding arts, micro-cracks must be expected in the heat-affected zone (fig. 10) and in the fadeout zone. Moreover, such cracks cannot be quantitatively ascertained with certainty by nondestructive methods with the present-day facilities. On the other hand, welded (instead of bolted) rotors cannot always be dispensed with, insofar as the aim is to achieve the required thrust/weight ratio. Under this compulsion to « live with cracks » fracture mechanics testing (K_{Ic}, crack propagation) and fractographic examination of joints with cracks are indispensible prerequisites as a basis for calculating a reliable design for the planned running time.

Further problems of materials mechanics are, for instance: the effect of repair welds on complicated castings and the quantitative effect of casting flaws and slag inclusions. We need these things to lay down material specifications and defect standards.

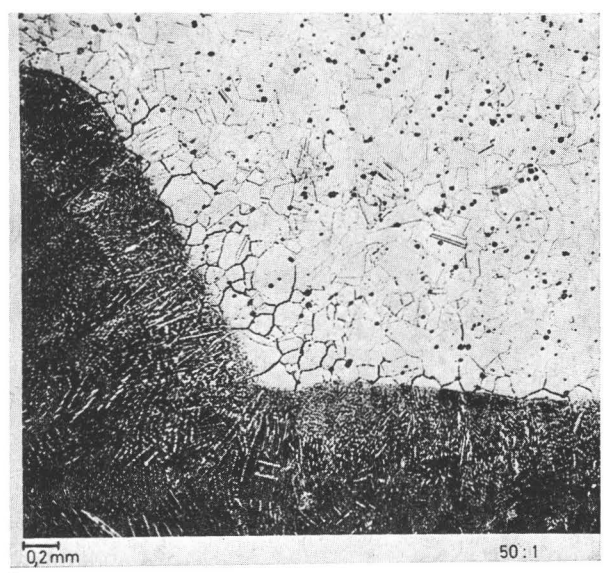

FIG. 10.

2.4. Subject Group 3: Improving engines and making them less expensive

Work covered by this group is of a short-term to medium-term nature and relates to engines which have already reached the prototype or production stage. Considerable experience is already available in running them, and there has been an opportunity to detect unpredictable weak spots. In an attempt to keep the

market for his engine as wide open as possible, the manufacturer comes under pressure price-wise, this prompting him to prune his design from the value engineering aspect. Finally, the basic version of a successful engine, is followed by derivatives which are characterised, for instance, by higher performance or adaptation to new requirements.

Work on materials towards these goals is, by its very nature, very closely related to specific engines and does not lend itself to the type of generalising portrayal aimed at here. Figure 11 therefore shows only the goals and, in a very general way, the engineering measures, substitution of materials, exchange of components, modification of components.

Let just one example serve to illustrate this value-engineering sector: the growing importance of titanium castings. I mentioned a considerable waste of material in the finish-machining of titanium forgings. By replacing such parts by castings, we are able to avoid this waste of material. Figure 12 shows, for example, an unmachined titanium casting destined for use as compressor casing in its finished state. It can serve as a good example of the progress which has meanwhile been made.

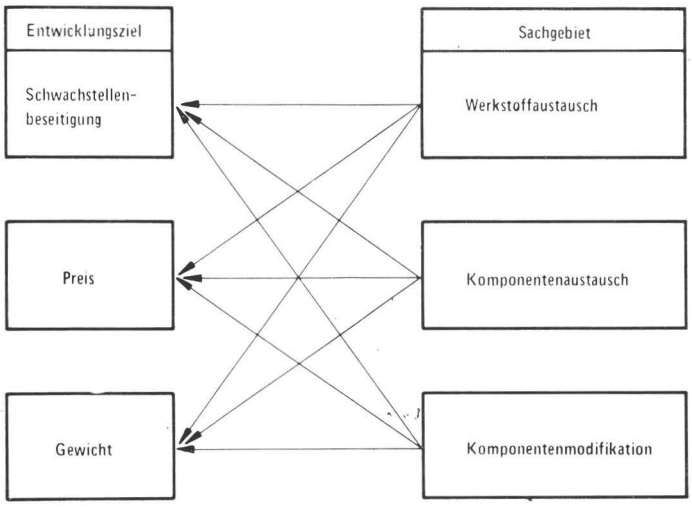

FIG. 11.

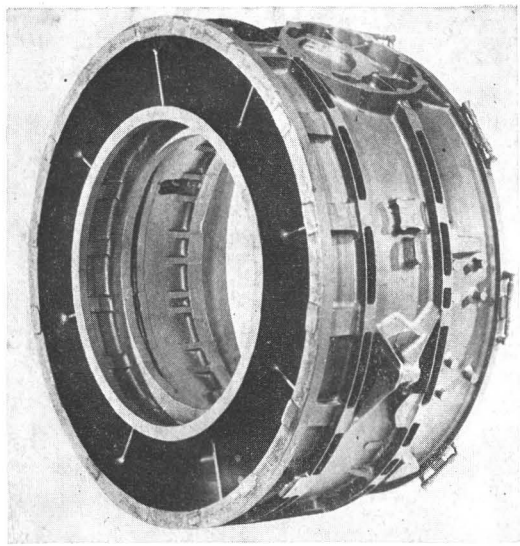

FIG. 12.

3. PRIORITY SCHEME

3.1. Necessity, difficulty, factors of influence

Because there is far more work to be done than one company could do, the necessity of a priority scheme for individual programmes is evident. The inhouse budget needs for « desirable » programmes on materials (exclusing process technology) can be estimated at up to ten million deutschmarks annually with the greatest ease. After the deduction of material costs, this represents a personnel requirement of some 150 staff. There can scarcely be a single European engine manufacturer capable of providing such a capacity simply for materials development. Unanimity is therefore very easily obtained on the need to do some pruning. The question of where this should be done is more difficult.

As no one is without his individual favourite topics and inclinations and, moreover, no one can oversee all the consequences, a priority scheme based on instinct, even in a discussion by a group of experts, is not objective and, therefore, questionable.

To objectivise however, a rating system is needed which must first be thought out and on which agreement must be reached, but experience has shown that agreement on the rating system is easier to reach than on direct ratings of the programmes.

3.2. Calculation scheme

The following formula should be taken as a basis for the priority P in the case under discussion:

$$P = \frac{(T.E)^{n_1}.D^{n_2}}{A^{n_3}} \qquad (1)$$

where

T : Technological progress for the engine.
E : Probability of success.
D : Urgency for the enterprise, measured on the basis of current projects and of the future manufacturing programme.
A : Estimated cost.

The relative importance of the fore-mentioned factors can be changed by means of the exponents n. However, their determination is very arbitrary without statistical material, especially in the relationship between n_1, n_2 on the one hand and n_3 on the other hand. To get round this difficulty, as a first approximation $n_1 = n_2$ were taken as $= 1$ and n_3 was taken as $= 0$, *i. e.* T, E and D were rated as equally important and the cost was left out of account. Thus, the simplified formula

$$P = T.\ E.\ D. \qquad (2)$$

was used.

Experience showed that there can be considerable divergencies and individual opinions in the assessment of technological progress. The difficulty was overcome, however, by using a composite factor to objectivise as well as was possible:

$$T = g_w.T_w + g_g.T_g + g_s.T_s + g_p.T_p + g_e.T_e + g_b.T_b$$

where

T_w : expected gain in thermodynamic performance (*e. g.* through an increase in gas temperature);
T_g : expected decrease in weight;
T : expected gain in reliability;
T_p : expected drop in cost of overall engine;
T_e : (for parts subject to wear) expected gain in service life;
T_b : improvement obtained, if any, in engine characteristics (*e. g.* acceleration behaviour).

The multipliers g are relative weights, which are attached to the factors T characterising the goals. As the goals differ according to each group of requirements to which the topics belong, the multipliers g differ from group to group. Ratings must, therefore, be given separately from group to group.

To give a numerical value to the various T factors, the following relative ratings are given within a topic group: to a development task, the goal conception of which was bound to bring about the biggest gain relative to a specific factor, ten points were given. The topic with the smallest gain (or even a loss) was given 0 points. Points between 0 and 10 were given to the other topics according to their relative importance for this factor.

Chart 1 shows an extract from a priority scheme, carried out in this way, on topics orientated towards the future (subject group 1), leaving aside the isolated factor D. The sequence of the rating may sometimes cause surprise. However, a retrospective analysis nearly always shows that the surprising result is not without its wellfounded logic.

It is clear to us that the method, in its details, still has an element of arbitrariness and is certainly open to criticism. However, it is doubtlessly more objective than a priority scheme based on « instinct » and at least has meant that previously highly divergent opinions have been reduced quite well to a common denominator. In practice, it has worked too well to be dismissed as a mere juggling with figures. The list of priorities has, of course, to be reviewed periodically and brought up to date.

4. NATIONAL AND INTERNATIONAL COOPERATION

By now, it should have become clear that work on all materials topics which are important for engine manufacture far exceeds the means of any single enter-

CHART I. — *Example of a priority scheme based on technical aspects (future-orientated materials development).*

Subject	Technical rating factors								T × E	
	T_W	T_G	T_S	T_P	T_L	T_B	$T = \sum_i g_i T_i$	E	absolute	normalized
g_i	10	7	6	8	5	4				
1. Static ceramic parts for small gas turbines.	10	5	2	10	4	7	275	9	2,475	100
2. Powder metallurgy for compressor discs.	3	3	7	8	4	5	197	9	1,773	72
3. Powder metallurgy for turbine discs.	4	3	6	6	4	5	185	9	1,665	67
4. New NDT methods for discs.	1	2	8	4	6	5	154	9	1,386	56
5. Rotating ceramic parts for small gas turbines.	10	5	2	10	4	7	275	5	1,375	55
. . .	.	.	.	.	.	.	.	.	.	.
8. New NDT methods for joints.	0	2	10	4	6	5	156	8	1,248	50
9. New NDT methods for blades.	2	1	10	4	6	5	169	7	1,183	48
. . .	.	.	.	.	.	.	.	.	.	.
12. Development of coatings against hot-gas corrosion.	5	1	8	1	4	5	153	6	918	37
13. Precision forging of titanium.	0	1	4	8	4	5	135	6	810	33
. . .	.	.	.	.	.	.	.	.	.	.
16. Directionally solidified turbine blades.	5	1	3	1	4	5	123	6	738	30
. . .	.	.	.	.	.	.	.	.	.	.
18. Measures against titanium burning.	0	0	8	3	7	10	147	4	588	28
. . .	.	.	.	.	.	.	.	.	.	.
. . .	.	.	.	.	.	.	.	.	.	.
24. Development of new titanium alloys with high hot-strength	0	4	3	3	4	5	110	3	330	13
. . .	.	.	.	.	.	.	.	.	.	.
26. Turbine blades made from refractory metals.	7	0	2	2	3	5	133	2	266	11
. . .	.	.	.	.	.	.	.	.	.	.

prise. Without closer examination, it can be assumed that this statement holds true for the aviation industry in general and for other industries too. To be in a position nevertheless to develop materials technology to the necessary extent, the single enterprise is bound to have recourse to international and national cooperation.

Examples of international cooperation in the sphere of materials technology certainly exist. The following have been singled out:

— Naturally the first that should be mentioned is Euratom, but there are further examples:

— The *joint British-German-Italian MRCA project*, borne by the ministries of defence of the three countries. The partners *Fiat*, *MTU* and *Rolls Royce* working together in Turbo Union are jointly developing the RB 199 engine for the MRCA combat aircraft.

— The Cost programme financed between 50 and 100 % by the European ministries for technology on materials and processes for engine manufacture.

The coordination of the separate programmes and exchange of information on these three programmes seems to be remarkably good. In addition, the Cost programme has a feature worthy of note: cooperation is taking place not only horizontally but also vertically, if the sequence Research Institute—supplier of materials—equipment manufacturer (user), is considered to be a vertical chain. In view of national cooperation, the latter point—in the opinion of the author an important one—is gone into in more detail:

The development of a material, until ready for use in production, usually takes place in three stages:

— development on a laboratory scale,
— transfer to full-scale manufacture,
— verification of reproductibility and determination of data.

In the course of this development, the focus of activities shifts from the research institute or development laboratory to the user. The success of a development idea and the time up to its practical exploitability depend very considerably on how good vertical cooperation on programme arranging is, as early as the first phase of development.

In practice, this means that the programme of work is oriented towards the future application right from the development phase taking place at the laboratory or institute level for which a good vertical flow of information, expedient work sharing and participation of suppliers of material and users in arranging the programme are prerequisites. In view of the growing scarcity of funds, this cooperation must develop beyond company boundaries.

Admittedly, a prerequisite is that the user companies have a clear concept of medium and long term planning for their development of materials. The priority scheme for development topics presented here serves this goal.

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 181-185

DISCUSSION

SECTION 1

S. F. Pugh. — These two papers have raised a number of fundamental problems which we should debate.

The power generating industry has given up the challenge of trying to produce superheated steam at 600° C. 600° C was a target, 575° C was a reality for a time, but quite recently in the U. S. A., steam temperatures were dropped to 550° C. Yet in the chemical industry apparently almost the same alloys in perhaps inferior form (cast) are working quite well at 1,000° C.

Perhaps some people here today have ideas why there is this great difference. Dr. Edeleanu mentioned that he is quite prepared to use tubes with a wall thickness of one inch, whereas in steam plant thin walls are used, partly from a feeling that materials will not stand up to the plastic flow necessary to accomodate the thermal stress arising out of the temperature gradient in the tube. Dr. Edeleanu is quite prepared to use a fairly brittle material an inch thick with large amounts of plastic flow caused by thermal stress. At 1,000° C, there must be almost complete relaxation of the stresses in the tube and hence a lot of plastic flow, and so I would like to hear the speakers try to reconcile these apparent contradictions.

Another point that has been raised is the importance of work on big rigs. Big rigs cost a lot of money and therefore they should be suitable for joint work. There are probably sufficient laboratory facilities for working on small specimens, but certainly not enough work on well instrumented rigs to get an idea of materials performance under the actual conditions of service. Very often in quite highly developed industries, materials are operating above the design temperature, and this is not realized. In the power industry certain types of failure were found which could not have happened at the design temperature.

A simple measurement showed that in fact these materials were operating at higher temperatures.

The importance of inspection has also been raised. One may want to know whether a material is becoming carburized, to what extent grain boundary corrosion has penetrated into the material and what is the thickness that has been affected. Laboratory research could indicate how to measure these things, preferably remotely. There are a number of areas of technical development where remote inspection is required; obviously the nuclear industry is one; and now there is in the U. K. the problem of inspecting rigs and undersea pipe-lines below hundreds of feet of sea water and covered with sea weed and barnacles. Dr. Edeleanu mentioned that it would be very nice to be able to monitor the performance of materials in his chemical plant without the need for cooling it down. Apart from saving time, it also reduces the number of thermal cycles. The life of an installation may be measured not in hours at temperature but in the number of times it is shutdown and allowed to cool.

Finally a question was raised about the relevance of mechanical properties to success in exploitation. For almost a hundred years boilers were designed on the yield stress criterion, and failed from corrosion. There is a lot of information on the properties of materials and yet 99 % of the failures in high pressure plant using both ferritic and austenitic steels occur in the welds, usually at places where the geometry is complex so that the stresses are not accurately known. Even less is known about the nature of the stress cycles that occur at those places when the pressures and the temperatures in the plant change.

Certainly we need to know more about the properties of welds and of heat affected zones.

In a recent survey the CEGB in the Midlands region examined 6,000 welds and found that something like 4,000 of them had flaws and something like 1,500 needed immediate repair. Obviously complex geometries and welds are very important problems on which to draw attention, because they are very often the weak points in performance and design.

I would like to take the first point: Why is it that the chemical industry can work up to a 1,000° C ? Why can they use thick pipes for heat transfer ? Why can they use cast materials with high carbon content ?

G. L. Swales. — For reformer tubes 18 to 20 mm is about the accepted maximum for that particular application because of thermal stress considerations. The main factor is the importance of a failure. The design of a catalyst tube furnace is such that in most cases one can isolate a failed tube, and that is an entirely different concept to what happens in a boiler. If you do get a failure of a steam reformer tube you do not necessarily have to shut down the furnace. Not all

designed reformers are the type where you can isolate tubes, but basically I think the fact is that the evolution in design and operation over the last 20 years has helped to use the materials at very high temperatures. If you are thinking of ductility, of course at operating temperatures, cast materials with high C contents have relatively high ductility; it is below 650° C or 700° C where they have relatively low ductility after service exposure. You can infer from some of those failures I showed of boiler water getting in and causing thermal shock cracking, that this is basically due to the fact that the material is cooled down to below the knee of the ductility-temperature curve.

S. F. PUGH. — In the austenitic steels and nickel alloys there is a trough in ductility at about 600° C to 650° C. At higher temperatures the ductility increases again. It seems that there are some similar points on corrosion. In one of the abstracts certain oxidation reactions were mentioned that do not happen at higher temperatures.

G. L. SWALES. — I should just make a point about the ductility of cast heat resisting alloys at temperatures below 650° C-700° C. I was talking about the high carbon alloys and not necessarily some of the other alloys which have relatively good ductility after extended service all through the temperature range.

And there are very critical applications outside the furnace, *e. g.* transfer lines, quench heat exchangers in ethylene plants and outlet headers in steam reformers, and there ductility is very important. Although wrought materials are used extensively, there are new cast materials which have been developed to have relatively high retained ductility.

L. W. GRAHAM. — I would like to try to answer Dr. Edeleanu's implied question as to why apparently in the Nuclear Industry it appears to be very difficult to operate at temperatures which seem modest compared with those common in the Chemical Industry.

Apart from the increas ngly stringent controls caused by safety and licensing factors on the nuclear side, which may have an imp ortant bearing, I will mention two particular features, namely insulation and heat exchangers. In the case of a Process Heat HTR, one of the main material and design problems to be faced is how to thermally insulate the pressure vessel from the primary helium coolant. I believe the main reason why the type of internal ceramic insulation mentioned by Dr. Edeleanu has not been considered is that once this part of the plant is installed, no opportunity exists to effect repairs during the life of the system (say, 30 years). I believe I am right in thinking that in the chemical applications such insulation systems are not expected to withstand this length of life and can be repaired should faults occur. Also I suspect difficulties may exist with impurities in the insulation being released into the coolant circuit.

However, having said this, it is my feeling that if we could achieve a reliable nuclear vessel insulation using the internal ceramic type mentioned by Dr. Edeleanu, then a real break-through would have been achieved. No progress can be made in this direction without much closer links between the nuclear and chemical industries. The second problem is the question of the heat exchanger design and the materials for the construction. In this meeting we are really talking about processes above 800° C being supplied with energy from the hotter primary coolant of a nuclear reactor generating 3,000 Megawatts of heat. Now that is approximately 10 times larger in its heat output than the largest ammonia plant operated in the world. You have to extract that heat from the reactor, put it into a process, and you have to do it in a very confined space. If you use one inch thick tubes as in a reformer, the reactor will be so large that it will just be an impossible economic proposition. The safety issues of a hot duct from the reactor to a process seem to me to be rather intractable. Therefore, in the nuclear process heat business you are probably facing the development of a compact heat exchanger design to operate at these high temperatures. Tubes for this would probably be no more than 25 mm diameter and 3 mm in wall thickness. For such tubes one would need strong wrought materials and again the requirement for very long lifetimes.

C. EDELEANU. — Could I please comment very briefly on this. First of all I agree with Swales: We do not use tubes more than one inch thick, 3/4″ is the normal. Cast tubes moreover are not or need not be brittle and it is time people ceased to think that castings are inferior products. They are not and especially so for high temperature applications.

On the thermal insulation problem we did start by thinking in terms of metallic internal insulation systems but it turns out that ceramic insulation is preferred because it is cheap, because it is simple, but primarily because it lasts indefinitely. If I had to design a vessel which has to last 100 years, I would not touch an internal metal insulation system. The one thing I do not like on the hot face is metal. You have to know how to design, how to match your expansion coefficients, how to deal with the cracks which will occur in ceramics but you can get very high reliability.

G. L. SWALES. — I wish to take issue with the concept that there is not a very important difference between 18 or 20 mm under heat transfer conditions and, say 25 mm. We design on hoop stress; the longitudinal stresses are theoretically 50 % of the hoop stress, but one has to add the longitudinal stresses due to thermal gradients. There have been reformers built with 28 mm, the intention being that they would be very safe, but they failed very rapidly because of circumferential weld failure. The important fact is that weld metals may have a high temperature rupture strength as little as 50-60 % of the parent material. If you have got thick tubes, it is quite possible that the longitudinal stresses are considerably in excess of this, nullifying the design safety factors leading in some extreme cases to premature circumferential weld failures.

The practice developed is that 18 or 20 mm is generally the designers' limit they tend to accept in current

design. One of the big problems of very small diameter tubes packed with catalyst is getting catalyst in and out. In fired heaters catalyst voids are a way of getting overheating, and that is a very important problem of design.

S. F. PUGH. — If there is 50 micrometers penetration down the grain boundaries, in a thin walled superheater tube in one year, then either this surface layer is depleted in chromium, or corrosion will continue at the same rate and the tube will fail completely in about 5 or 10 years. It is a rather different problem with thick walled cast tube.

H. WALTHER. — Among the many problems which Dr. Edeleanu gave the metallurgists to solve, an important one is the finding of non-destructive methods which would work during service at high temperature and which would give us an idea of the residual life of a reformer tube or another component.

I would like to ask the designer and the plant operator and perhaps the metallurgist to help each other a little bit in solving this problem. In order to find or to improve non-destructive testing methods, it would be desirable to put into a reformer tube a sample which simulates rather well the operation conditions as temperatures and stresses. A shut down would be required, not of 10 days, but just enough to take out and test the sample.

C. EDELEANU. — Plant experiments are very expensive, but they can be done. If you have a technique which shows promise, I would be delighted to make these facilities available. It would however be very difficult to simulate the experience of the 400 tubes of a furnace and there is a sampling problem. Moreover there is a factor 10 in the properties between different castings. So the problem of monitoring by surveillance technique of this kind is not too easy. But if one can come up with the principles of a technique, we would obviously look at it.

H. WALTHER. — Thank you for the answer. We would need however from the operators some more information, for instance, if one should monitor the welds. The question is not so much how fast the material deteriorates around the weld, but perhaps how initial cracks in the weld behave. They are there, and one wants to be sure that they do not propagate. In other components the deterioration of the material is different, this is in the structural long range order, for instance in the dimension ranges where the precipitates play a role in order to stop the dislocations. Also in these regions methods are available. There are very modern low angle scattering techniques, they provide such possibilities, and I would like to take your answer as an encouragement to continue this way.

C. EDELEANU. — Obviously I will encourage you. I suggest you pay a visit to a reformer plant: You are welcome to our place, you will then get an idea of what is feasible there.

R. A. U. HUDDLE. — What I think is important is to study the mechanisms of failures. If we go back to aircraft, we know that the Comet failed on fatigue, whilst it was designed on proof stress. In most high temperature plants the basic design parameter is stress rupture life in air. However, they do not fail by stress rupture, they fail through fretting, fatigue, etc.

In the paper that I am presenting later, I deal with this specifically. I think Dr. Walther has raised a very important question: Can you give us that help to come to grips with the real problems ? What we want to know are the problems that are common to the industries throughout the Community. I hope you can think about this and make some worthwhile suggestions for experimental investigations. For example can you send us a failed reformer tube which can be cut up and investigated ?

M. VAN DE VOORDE. — Table I of Dr. Swales' paper shows a number of materials. How many of these materials have been developed specially for the chemical industry ? Was it necessary to do some development work in this field ?

G. L. SWALES. — Let us take the cast alloys. Of those only three have been developed with the petrochemical industry firmly in our mind. IN 519 was an optimization programme around HK 40, that was specifically aimed at as a reformer tube material not too different in cost but optimizing strength and ductility. The 32/30 niobium material was developed to solve the problem of header failures which I showed in a picture.

Nickel 30 chrome was a development specifically by one foundry in Germany for carburization resistance. Out of that list of cast alloys therefore there are 3 which had been developed purposefully. In the case of the wrought alloys I do not think Alloy 800 N was specifically developed for the petrochemical industry (the other industries have been very interested in that development as well), but of course the petroleum and chemical industry were very much in mind and, being important users of it, set the scene for that development. Incolay 802, I think I am right in saying, was specifically aimed for the ethylene market, but of course there are other applications for the alloy as well. So summarizing: A certain amount of this alloy development has been specifically aimed for petroleum and chemical applications.

M. VAN DE VOORDE. — I understand from your paper that you possess enough creep data for design purposes. Has this data been obtained in relevant environments and in which institutes in Europe has this research been carried out ?

G. L. SWALES. — The stress rupture data of many of these alloys have been developed over the years by the foundries and wrought alloy producers studying some of their own products and also by research associations under sponsorship by industrial groups. Various

organisations have tried to take a lot of this data and put it in plots and get an idea of the scatter and so on.

That is generally how the data is being developed. There has been very little data from creep tests in environments. The cost of it is very very high, and industrial commercial pressures have often generally stopped that work being done. I think it is a very important area. In many of the applications we have learned what happens in environment by experience, but with new concepts you do not want to try it for too long.

W. BETTERIDGE. — I want to take up Mr. Swales' plea for pilot rig tests and Dr. Edeleanu's comment that existing creep data are perhaps more than adequate and that it is difficult for the designer to use those specifically as design data. I think the situation can be compared with fatigue testing which conventionally was carried out on smooth polished test bars machined from wrought bar in the direction of working. But nobody nowadays can really apply those fatigue data except to compare the relative properties of different materials. They cannot use them as direct design aids as applied to a component; you must do fatigue testing on a specific component. There are at least three factors that affect the properties: the metallurgical structure of the large component as compared with the small wrought bar, the effect of internal stress in the component arising usually from heat treatment or machining, and finally the stress distribution and concentration that arise in a relatively complex component. That is why you have to do component testing to assess the fatigue properties. I would like to plead that very similar conditions now apply to creep testing and that creep testing in a uniaxial direction on a simple wrought bar does not give you very much indication of the direct stress which a component could carry. Again the metallurgical considerations of unidirectional or multidirectional stresses, along or against the direction or working of wrought material, or against the direction of grain growth in cast material, are all factors that affect the application of the results. In the same class one can put the environment effect, relating the extent of exposed surface in relation to stressed area of the component, which is covered by the environmental creep testing that, for example, Dragon has been carrying out. So I make a plea to drop the use of stresses and to turn to the use of applied loads on specific components as the criterion.

S. F. PUGH. — I think these papers have given the general impression that in the established technology the materials of interest are all based on iron-nickel-chromium ternary alloys where chromium confers oxidation resistance and nickel is there to give the strength, and there seems to be no utilisation of any other alloys. We have to discuss at this conference whether there are any other materials that would compete under certain conditions. It is not only temperatures and stresses but also the environment which is of importance.

Are there any other ranges of materials which might be of interest at high temperatures ? Are there any requirements or conditions to meet which are outside the range which could be met by the iron-nickel-chromium system ? Another point that has been raised was the technique of cost benefit analysis for research.

Namely to decide on the objectives of the programme, the time scale, the costs, what is the likely commercial benefit of success and what is the probability of success. I think that the working party on high temperature materials research will be well advised to quantify their cost benefit analysis.

W. BETTERIDGE. — One of Dr. Davidson's slides included the cobalt-base alloy Umco 50, but he did not mention its good wear resistance at furnace temperatures. The alloy was largely developed to meet that requirement, and I am not clear whether that characteristic is associated with the high percentage of hard carbides present or with the structure of the matrix, which is hexagonal, at least at normal temperatures. With additions of molybdenum the transformation temperature of cobalt from hexagonal to cubic is pushed up in the region of operating furnace temperatures. I think this is a field in which some interest lies. Some investigations could usefully be carried out on the influence of the structure of matrix and of second-phase particles on hot wear resistance. There are other alloying elements which stabilize the hexagonal structure much more than molybdenum does, and although these are expensive they may well be worthwhile.

The other aspect I would like to comment on, is that of electrical resistance elements. In the metallurgical industry scale flaking is perhaps not very important in terms of its effect on the materials being processed, but in the glass and ceramic industry where electrical kilns are quite widely used, scale flaking is a very serious problem. Little bits of chromium-containing scales falling on decorative pottery can ruin a complete furnace load. Therefore the influence of minor elements, not only rare earths but also silicon, calcium, zirconium and other materials have, as Dr. Davidson said, a very marked influence on scale adhesion. Their presence in materials for ceramic kilns is an extremely important factor. It may be well worth a further study.

H. WALTHER. — I wish to address a question to Dr. Davidson concerning gamma-prime hardening. When you plot a strengthening property in function of the titanium plus aluminium content, perhaps one should take account of the fraction of titanium which has reacted with carbon and precipitates as carbide. I would like to mention that just now we had some success in plotting aluminium plus titanium minus four times the weight fraction of the carbon assuming that the carbon content has allowed the titanium to precipitate, and we succeeded in getting smooth curves. Did you do something in this direction ?

J. H. DAVIDSON. — I ought to stress that the slide which you are referring to is very approximate. I do not think that multiplying the carbon by four would make a significant difference to the titanium level.

R. A. U. HUDDLE. — Some years ago when I was working in the Dragon Project, we looked at aluminium containing alloys, as we were aware that if one could get an alumina film, it was certain to have an optimum effect. We also looked at silicon containing alloys. However, we found these alloys were very difficult to fabricate when one has concentrations of aluminium where its effect is significant. Are the alloys that you are referring to capable of being fabricated into components that could be used in heat exchangers, etc. ?

J. H. DAVIDSON. — I think aluminium is probably easier to introduce into electrical heater materials, in which there are fairly low solid solution strengthener levels than into heat resisting alloys for stress bearing applications because aluminium has a very strong tendency to promote the sigma phase formation.

S. F. PUGH. — In the ferritic steels we in the UKAEA are developing an iron-chromium-aluminium-yttrium alloy which can be fabricated in thin foil form. It has an extremely protective alumina film; grades are available for use up to 1,300° C in air. These are all extremely weak materials at high temperatures and applications are limited. In heat exchangers where there are large pressure differentials, they would probably be unsuitable.

R. A. U. HUDDLE. — Could you make, say 25,000 km of high quality thin walled tube for a 3,000 Megawatt heat exchanger at a reasonable price ? That is what we must have.

S. F. PUGH. — We are making 50 ton melts now and mass producing in sheet form, but not in tube form. It is probably best to use this material only as a coating for oxidation resistance.

M. VAN DE VOORDE. — I would like to ask Dr. Esslinger a question. Since reliability is very important to your components, are you undertaking research to enable you to predict component life time, on the basis of data collected on a laboratory scale ?

P. ESSLINGER. — Yes, naturally that is our daily bread. It is of course depending on the component; mostly we do it from crack propagation and from LCF and HCF.

M. VAN DE VOORDE. — What kind of development work is being done on ceramics, except coatings ?

P. ESSLINGER. — In Germany we have a fairly large programme on ceramics for small gas turbines for automotive engines. We look not only for rotating parts like turbine wheels but also, and it seems to be more promising, for static parts, for example, combustion chambers and so on. In my opinion in about 5 or 10 years time applications may be possible, but only for vehicles on the ground, not in the air.

FIRST PETTEN COLLOQUIUM
ON
ADVANCED HIGH TEMPERATURE MATERIAL:
TECHNOLOGICAL AND INDUSTRIAL ASPECTS (*)

SECTION 2

REQUIREMENTS OF HIGH TEMPERATURE REACTORS AND THEIR ADVANCED APPLICATIONS

(*) The *1st. Section* of proceedings of that *Colloquium*, organized by the *Commission of the European Communities* on January 29 and 30, 1976 in Petten (the Netherlands), as be published in the *Revue Internationale des Hautes Températures et des Réfractaires* 1976, *13*, nº 3, pp. 139-185 ; *Section 4* and *List of Participants* will be published in 1977, *14*, nº 1, pp. 5-62.

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 190-203

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MATERIALS FOR ADVANCED HIGH TEMPERATURE REACTORS

By

L. W. GRAHAM (*)

1. *INTRODUCTION*

Ever since the original concept of a Helium Cooled High Temperature Reactor in the 1950's, the system has been heavily dependent on materials inovation and development carried out hand-in-hand with the application of sound engineering principles. In the first instance, the whole concept depended on the development and application of a core capable of delivering coolant at temperatures well able to better those available from other nuclear reactors, matching the steam generating conditions of the most modern fossil fired electricity generating stations. To achieve this the by now well-known fission-product retaining coated particle fuels were developed [1 and 2] together with a firm basis for the engineering application of graphite in the core [3 and 4]. Also the successful operation of the experimental Dragon Reactor and the plants at Julich and Peach Bottom have demonstrated the basic engineering principles of the helium cooled reactor. These principles are incorporated in the commercial exploitation of the HTR for power operation through the steam-cycle.

Even in the early days of the High Temperature Reactor, however, it was always realised that the use in conventional steam raising did not represent the end point in the development of the system but a stepping stone to more efficient and varied applications. Early attention was directed towards the Closed Cycle Helium Turbine [5] and this is now in the first stage of exploitation. More recently the potential of the HTR as a source of process heat is being vigourously pursued [6 and 7].

1.1. The Helium Gas Turbine

The direct cycle helium gas turbine has been the subject of many design studies over the last ten years. At a *Dragon Project Colloquium* in 1965 [8] the basic arguments favouring the direct cycle were stated, and experience with closed cycle air turbines over the previous 25 years was described. Several proposals for HTR gas turbines (HTR-GT) were also discussed. In 1966 Bohm [9] presented a design for a prototype 22 MW(e) system with helium entering the turbine at 675° C, and suggested that his basic scheme was suitable for power plant in the 1,000 MW(e) range.

Later, Hosegood *et al.* [10] reported the Dragon Project Engineering studies on the Direct Cycle HTR, giving their detailed design for a 980 MW(e) power station with a helium inlet temperature of 967° C. This report has been followed by studies by GEC Gas Turbines Ltd. in the UK [11], by *General Atomic Company* in the USA [12, 13, 14] and by the *HHT project* in Germany [15].

These designs proposed turbine inlet temperatures in the range 800-850° C. The earlier designs [10, 11, 12, 13] suggested vertically mounted turbomachinery which would take full advantage of the established pod layout of pressure vessels. The later proposals [14, 15] have favoured more conventional horizontal turbines to minimise development of new technology. The main details of each design are shown in table I.

It is likely that an early direct cyle HTR would operate at the lower temperatures rather than those suggested by Hosegood *et al.* However, the benefits of the direct cycle improve with increasing temperatures, and with the incorporation of a bottoming cycle, efficiencies of approach, 50 % could be achieved. Most attention is now therefore directed to the development of systems with turbine inlet temperatures above 900° C.

1.2. The HTR as a Source of Process Heat

A concise but useful summary of the direct application of nuclear heat in chemical industry was given recently by White [16]. This article discusses the poten-

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tial for nuclear process heat, and the HTR process heat in particular, but also notes the problems of linking an HTR to industrial establishments in their present form.

TABLE I. — *Main Design Features of Commercial HTR-GT Proposals (Dry Cooled).*

	Dragon (1970)	GEC (1972)	HHT & GA (1975)
Thermal Output (MW)	2,208		3,000
Electrical Output (MW)	980		1,070
Overall Efficiency (%)	44.4	41	36
No of Turbine Loops	4 (*)	4	3
Orientation of Turbomachinery	Vertical	Vertical	Horizontal
Rating of each generator (MW)	500	300	370
H. P. Turbine Inlet Temperature (°C)	967	827	816-850° C
H. P. Turbine Outlet/L. P. Turbine Inlet Temperature (°C)	762	657	
L. P. Turbine Outlet/Recuperator Inlet Temperature (°C)	549	502	548
H. P. Turbine Inlet Pressure (bar)	59	49	60-70
H. P. Turbine Outlet/L. P. Turbine Inlet Pressure (bar)	37	30	
L. P. Turbine Outlet/Recuperator Inlet Pressure (bar)	20	18	31

(*) 2 double flow units.

Apart from safety aspects, the main problem with nuclear process heat is essentially one of scale. The output of a 3,000 MW nuclear reactor is ten times greater than the maximum power requirement of the largest ammonia plant in the USA. The other factor that would make it difficult to supply heat directly to the chemical process industry is the time that a nuclear reactor is out of service. Nuclear reactors are reliable compared with conventional power stations, but even an outage rate of 20 % can lead to unacceptable cost increases for most chemical processes.

These problems of scale and availability are bypassed if the nuclear heat is used to produce a secondary fuel. Of several possible process heat applications for the HTR, three have received considerable attention:

a) production of hydrogen by reforming reactions between water and hydrocarbons, particularly methane;

b) steam or hydro gasification of coal; and

c) production of hydrogen by thermal decomposition of water.

These processes were discussed recently in series of papers presented at Conferences in Paris [17], London [18] and Jülich [19].

As with the direct cycle helium turbine, the efficiency of process heat installations increases rapidly with temperature. The minimum heat supply temperature for steam reforming methane is about 800° C, but higher temperatures are needed for the direct gasification of coal. These temperatures are similar to those required by the most recent proposals for direct cycle gas turbines (table I), but the need for an intermediate heat exchanger would increase temperatures in the primary circuit to well above 850° C.

2. MATERIALS SELECTION

In these more advanced applications then, bulk helium coolant temperatures in the range 850° to 1,000° C must be considered. It is very evident that, although work must continue on the fuel and core materials, considerably more emphasis is needed on structural materials and components of the primary circuit and associated process plant to ensure sucessful development and commercial exploitation. The nuclear industry has special features in relation to materials technology and plant reliability. These pose problems which are of especial importance in advanced HTR applications because of the high temperatures involved. Some of the features and their implications are set out below.

Special nuclear features

High Capital Cost of Plant.
High Cost of Plant Outage.
Possible Inaccessibility of Components.
Difficulty and Cost of Maintenance.

Implication

High Importance of Reliability and Safety of Materials Performance.

While these features are not peculiar to the High Temperature Reactor, the fact that phenomena such as solid state diffusion depend exponentially on temperature means that the problems of selecting materials and determining their long term behaviour are especially critical in advanced HTR applications. Additionally, due to the special nature of the environment, unusual surface and structural effects may be found. The basic issues in the behaviour of metals are then as stated below.

Metals behaviour in HTRS

High Temperature Metallurgical Stability.
Effect of Environment on Corrosion Properties.
Effect of Combined Influence of High Temperature and Environment on Structure and Mechanical Properties.

HTR helium possesses features which can have important implications on the behaviour of metals and alloys. The sources of impurities and their levels have been discussed in detail in reference [20]. Briefly, the reaction of impurities with the very hot core graphite, together with a radiolytically aided formation of methane from hydrogen, leads to a balance of impurities having the following main features. Firstly the hot reactor core graphite removes all oxygen but the slower kinetics of other reactions leads to small traces of water, carbon monoxide, carbon dioxide and hydrogen. Due to the in-core reaction of the hydrogen some

methane is formed and there is a small level of residual nitrogen from the degassing of the graphite.

Estimates of the conditions expected in advanced HTR's which are in keeping with the experience of operating the Dragon Reactor, lead to the conclusion that when expressed in micro-atmospheres:

the H_2/H_2O ratio will be 500,
the CO/CO_2 ratio will be 50,
and the H_2/CH_4 ratio will be 10

and the oxygen partial pressure will be 10^{-24} atm.

The thermodynamic implications of these compositions have been discussed previously [20] but in general one has a situation in which the absence of oxygen prevents the formation of conventional protective films. However, the low levels of oxidising and carburising species opens the way for selective oxidation to occur as well as a simultaneous carburisation.

3. MATERIALS BEHAVIOUR

3.1. Experimental Methods

In the following, results recently obtained from the Dragon Programme will be presented to illustrate materials behaviour. The experimental work is focussed on the exposure of specimens under constant load to study the long-term creep behaviour in simulated HTR Helium [21]. To allow a very wide range of materials to be studied under these conditions two large rigs are used, each of which contains over 1,000 specimens disposed in « stringers » contained in furnaces operating up to 1,000° C. The stringers of specimens are exposed to flowing HTR helium generated in a storage loop which has take-off and return points for each furnace. Creep measurements are made at intervals on the individual specimens on removal from the furnaces, and specimens are also removed for detailed examination providing correlation between the mechanical behaviour and structural changes.

The concentration of impurities used in the tests and typical levels in the Dragon Reactor are shown in table II.

TABLE II. — *Helium impurity levels used in the Dragon Metals Programme.*

Test Facility	Impurity levels in µatm.					Pressure in atm abs.
	H_2	CO	H_2O	CH_4	N_2	
Dragon Reactor						
(*a*) Normal running conditions . .	10	3	1.0	1.0		20
(*b*) With water injection . . .	200	40	4.0	10.0		20
Rig tests-						
A (1969-1971). .	54	36	9.0	—		1.8
B (1972-1974). .	50-100	25-50	0.5-3	3-8	⩽ 11	1.8
C (1975-). .	500	50	1.5	50	⩽ 11	1.8

Comparative tests were conducted in air. Most specimens were of 4.5 mm diameter and 22.6 mm gauge length but 6.4 mm diameter specimens were used for cast alloys. Gauge lengths were marked with indentations between which creep strain was measured, usually at 1,000 hours intervals. The indentations also served to provide an indication of notch sensitivity in wrought alloys. Cast alloys were marked on the shoulders to avoid premature failure induced by a notch.

Specimens were also weighed at the measurement intervals. In the early stages of the programme, weight change data were recorded from stressed samples and were necessarily approximate. More recently, however, the measurements have been made on corrosion samples only and are of much greater precision.

3.2. Materials

In table III are listed materials which are of current interest in the work on advanced HTR systems, together with an indication of their application. Compositions are given in table IV.

A small number of alloys has been selected for each component or class of components to provide an initial reference or basis for comparison. There are mostly well established commercial alloys that, from the results of the previous tests by Dragon, would be expected to behave reasonably well in HTR helium. At this stage it has been assumed that alloys containing substantial additions of cobalt or tantalum would not be chosen for use in the primary circuit of an HTR. Thus, alloys containing more than residual levels of these elements have been excluded from the list of reference alloys for the primary circuit. However, many of the alloys in this category have better mechanical properties than the reference alloy and they are being examined to see whether the behaviour of the oxide films might in the end allow use in an HTR.

3.3. Effect of Temperature on Oxidation and Carburisation in HTR Helium

In any oxidising or carburising environment, reaction rate would be expected, from kinetic considerations, to increase with temperature. However, the oxides and the carbides of metals become less stable at higher temperatures (*i. e.* their free energy of formation becomes less negative) through the relations $\Delta G_{ox} = RT \ln p_{O_2}$ or $\Delta G_c = RT \ln a_c$.

Eventually a temperature (the dissociation temperature) is reached above which these compounds cannot form. Here ΔG_{ox} is the free energy of oxide formation, Gc that for carbide formation, p_{O_2} is oxygen partial pressure, a_c is carbon activity, R is the gas constant and T is absolute temperature.

Most high temperature alloys have been developed for service in air (high p_{O_2}) where dissociation temperatures are well above the melting point of the alloys. Oxidation resistance therefore relies on formation of

TABLE III. — *Major high temperature components of advanced HTR systems and possible constructional alloys.*

Components	Reference alloys	Reason for choice of reference alloys	Lower priority alloys
Turbine blades and vanes	713LC M-21	Strength at high temperatures without undesirable elements	Nimonic 80A Nimonic 90 Nimonic 115 Udimet 520
	TZM-Molybdenum	Strength at very high temperatures and resistance to corrosion in HTR Helium	MAR-M 004 IN-738 M-21Z M-22 IN-591 IN-100 Udimet-700 MAR-M 247 NX-188 Dispersion-strengthened alloys
Turbine Discs	A-286 Inconel 706	Well established disc alloy Good fatigue strength	Rene 95 Waspaloy Advanced powder met. alloys
High Temperature Ducts, Casings and Linings (Primary Circuit)	Mastelloy X	Well established alloy with only low level of Co	Alloy 800 Incoloy 800H Incoloy 802 Incoloy 807
	Nimonic 75	Well established alloy, used for construction of ducts in Dragon reactor where it showed good behaviour	Incoloy DS Nicral K Sanicro 32X Inconel 600 Inconel 617 Inconel 625 IN-102
	IN-586	Early tests have shown good properties in impure helium	Hastelloy S Paralloy CR32W HK-40 Manaurite 36X
	IN-519	Cast austenitic steel with good strength and microstructural stability. Contains niobium which should give good corrosion resistance in HTR helium	TZM Molybdenum
Intermediate Heat Exchanger Tubes.	Hastelloy X	As for Primary Circuit	Alloy 800 Incoloy 800H
	IN-586	As for Primary Circuit	Incoloy 807 Incoloy DS Sanicro 32X Inconel 600 Inconel 617 Inconel 625 IN-102 Hastelloy S
Duct to Process (Secondary Circuit)	Hastelloy X	As for Primary Circuit	As for primary circuit ducts, etc.
	Nimonic 75	As for Primary Circuit	
	IN-586	As for Primary Circuit	
	IN-519	As for Primary Circuit	
	Inconel 617	Ni base alloy with good structural stability and long term strength	
	Incoloy 807	Wrought austenitic steel which has shown good corrosion resistance in impure helium in early Dragon tests	

protective films. Similar considerations apply to alloys developed for carburisation resistance in atmospheres such as hydrocarbon reformers.

As described previously the essential feature of the helium coolant of an HTR is its high purity. Levels of oxidising and carburising species in the coolant are very low and Huddle, Kofstad and Pearce [22] and Pearce [23] showed that dissociation temperatures of oxides and carbides of iron and nickel will be well below operating temperatures of HTRs. Other compounds would have dissociation temperatures close to operational ranges of advanced plant. For example, chromium is not expected to oxidise or carburise above about 1,000° C.

Dixmier, Willermoz and Roche [24] reported corrosion behaviour that appeared to support this suggestion since oxidation of several nickel base alloys was less severe at 900° C than at 800° C. Recent work by Dragon Project has provided further support. Figure 1 shows that surface oxide depth on AISI 321 steel fell almost to zero after exposure at 1,000° C for 500 hours in helium. Results for other alloys are also included. This diagram is considerably simplified and contains data from three gas compositions (table II). These variations, together with variations in alloy composition within specification ranges, will slightly affect the positions of the curves although their shape is unlikely to be altered greatly.

TABLE IV. — *Typical compositions of test materials.*

Alloy Type	Alloy	C	Ni	Co	Cr	Fe	Al	Ti	Mo	W	Nb	B	Zr	Others
Wrought Ni-base	Nimonic 75	0.13	Bal		19.5	2.0		0.4						
	Nimonic 80A	0.06	"	1.0	20.5		1.4	2.05						
	Nimonic 90	0.09	"	16.5	19.5		1.4	2.35						
	Nimonic 115	0.16	"	13.2	14.2		4.8	3.7	3.2					
	Udimet 520	0.05	"	12.0	19.0		2.0	3.0	6.0	1.0		0.005		
	René 95	0.15	"	8.0	14.0		3.5	2.5	3.5	3.5	3.5	0.010	0.05	
	Waspaloy	0.08	"	13.5	19.5		1.3	3.0	4.3			0.006	0.06	
	Hastelloy X	0.10	"	1.5	22.0	18.5			9.0	0.6				
	Hastelloy S	0.02	"		15.5	1.0	0.2		14.5					
	IN-586	0.05	"		25.0				10.0					0.03 Ce; 0.015 Mg
	Inconel 600	0.04	"		15.8	7.2								
	Inconel 617	0.07	"	12.5	22.0		1.0		9.0					
	Inconel 625	0.05	"		22.0	3.0	0.2	0.2	9.0		4.0			
	IN-102	0.06	"		15.0	7.0	0.4	0.6	3.0	3.0	3.0	0.005	0.03	0.02 Mg
Cast Ni-base	713LC	0.05	Bal		12.0		5.9	0.6	4.5		2.0	0.010	0.10	
	MAR-M 004	0.05	"		12.0		5.9	0.6	4.5		2.0	0.010	0.10	1.3 Hf
	IN-738	0.11	"	8.5	16.0		3.4	3.4	1.75	2.6	0.9	0.010	0.04	1.75 Ta
	M-21	0.10	"		6.0		6.0		2.0	10.5	1.5	0.02	0.10	
	M-21Z	0.10	"		6.0		6.0		2.0	10.5	1.5	0.02	0.50	
	M-22	0.13	"		5.7		6.3		2.0	11.0			0.60	3.0 Ta
	IN-591	0.10	"	12.0	3.0		5.7			19.0		0.03	0.37	3.0 Ta
	IN-100	0.18	"	15.0	10.0		5.5	4.7	3.0			0.014	0.06	1.0 V
	Udimet 700	0.08	"	18.5	15.0		4.3	3.5	5.2			0.03		
	MAR-M 247	0.15	"		8.5		5.5	1.0		10.0				3.0 Ta; 1.3 Hf
	N x-188	0.04	"				8.0		18.0					
Wrought Fe-base	Alloy 800	0.04	32.5		21.0	Bal	0.4	0.4						
	Incoloy 800H	0.08	32.5		21.0	"	0.4	0.4						
	Incoloy 802	0.35	32.5		21.0	"	0.6	0.75						
	Incoloy 807	0.08	40.0	8.0	20.5	"	0.35	0.45		5.0	1.0			
	Incoloy DS	0.05	37.0		18.0	"								2.3 Si
	Sanicro 32X	0.07	31.0		21.0	"	0.35	0.35		3.0				
	A-286	0.05	26.0		15.0	"	0.2	2.0	1.3			0.015		
	Inconel 706	0.03	41.5		16.0	"	0.2	1.0	0.5		2.9			
Cast Fe-base	IN-519	0.3	24.0		24.0	Bal					1.5			
	HK-40	0.4	20.0		25.0	"								
	Paralloy CR32W	0.1	32.0		21.0	"					1.0			
	Manaurite 36X	0.4	33.0		25.0	"					1.0			
Molybdenum	TZM	0.015						0.45	Bal				0.09	

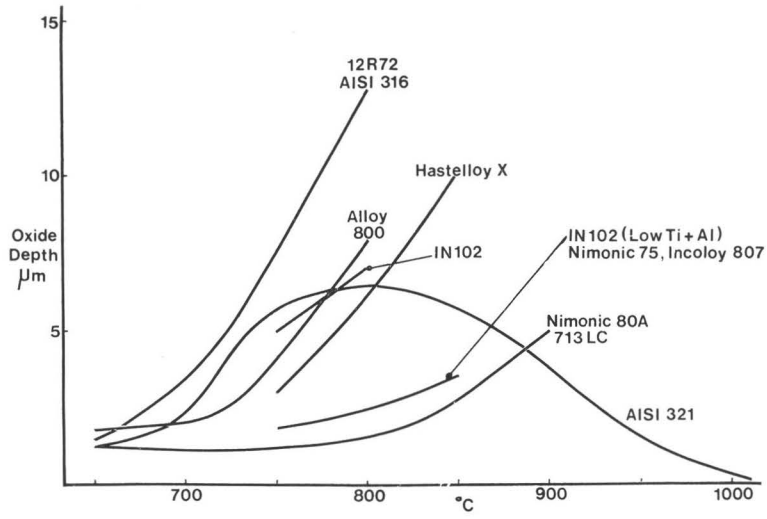


FIG. 1. — *Surface oxide depth vs. temperature for various alloys after 5,000 hours in HTR* He.

AISI Type 321 Steel. — Parts of five environmental test furnaces used by the Dragon Project were made from 2 mm diameter wire of AISI type 321 steel. Individual furnaces had operated for about 5,000 hours at 650° C, 700° C, 800° C, 900° C and 1,000° C. As shown in figure 1, the thickness of the surface oxide increased with temperature to about 800° C, but then decreased to zero at about 1,000° C. This can be seen in the microsections, figure 2, which also show increasing intergranular oxidation up to about 900° C, with little or none at 1,000° C. The measurements were consistent with those obtained on

the type 321 test material (Code D1) [25], up to 800° C and the latter data have also been used in compiling figure 1.

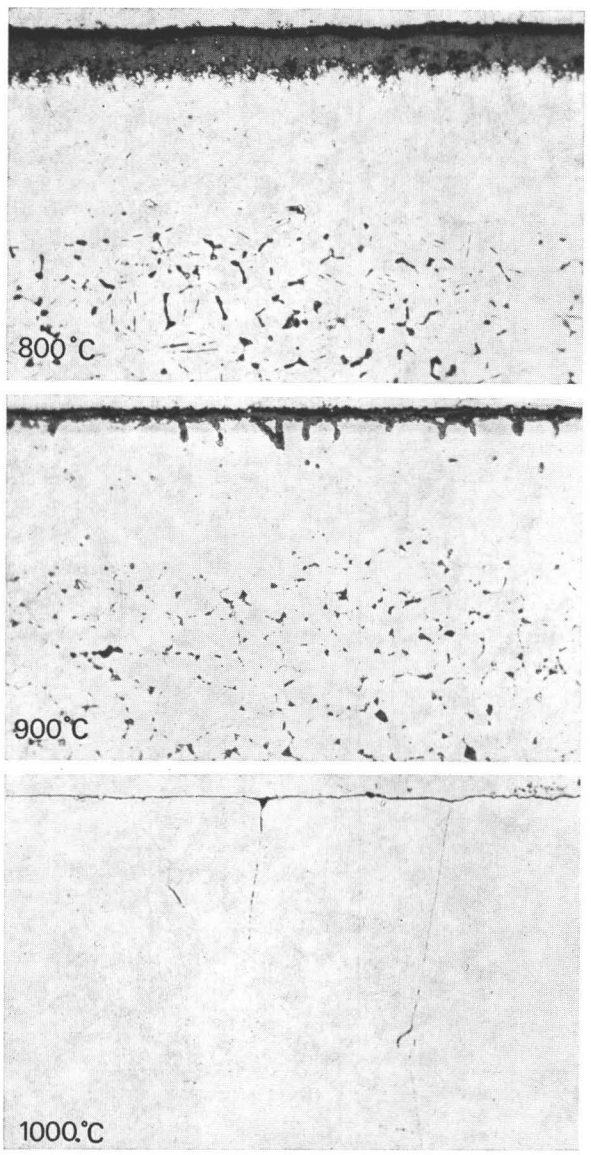


FIG. 2. — *AISI type 321 steel exposed for 5,000 hours in HTR helium.*

The absence of Cr_2O_3 at 1,000° C enables the equilibrium oxygen partial pressure in the gas to be estimated from free energy data as about 10^{-21} atm or less. Conversely, for Cr_2O_3 to form at 800° C, as was the case, the equilibrium p_{O_2} must be greater than 2×10^{-27} atm. Both calculations assume a chromium activity of 0.2 for the steel. Thus the value of p_{O_2} in the furnace can be estimated as $10^{-24\pm3}$ atm at 800-1,000° C.

Figure 3 summarises the extent of both oxidation and carburisation in these components. Figure 3*a* shows the depths of surface and intergranular oxidation. The difference in the temperatures for the maximum rates of surface and intergranular oxidation can be ascribed to the presence of different oxide forming elements in the two cases. Pearce [23] showed that in Alloy 800 the surface scale was principally a chromium-

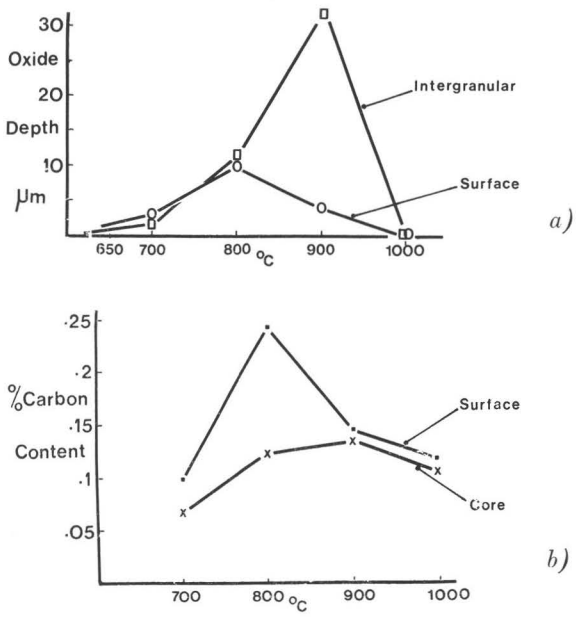


FIG. 3. — (a) *Variation in oxide depth of AISI 321 after 5,000 hours in HTR* He. (b) *Variation in carbon content of AISI 321 after 5,000 hours in HTR* He.

manganese oxide, whereas intergranular oxides were rich in aluminium and titanium. The greater stability of TiO_2, relative to Cr_2O_3, requires that even assuming a titanium activity of 0.01 in AISI 321 steel, TiO_2 would cease to form at 900° C only at $p_{O_2} \sim 8 \times 10^{-29}$ atm which is less than that calculated from above. At 1,000° C, however, TiO_2 would cease to form at $p_{O_2} \sim 10^{-26}$ atm and once again it is reasonable that intergranular oxidation should be vanishing at this temperature.

The carburisation of the furnace components was examined by machining a surface layer about 0.3 mm deep from each. The carbon contents of this layer and the remaining core are plotted in figure 3*b*. Slight carburisation had occurred at 700° C. At 800° C the carbon content of the surface layer (0.24 %) was about four times that of the initial material. At 900° C and 1,000° C the carbon content was uniform throughout the specimen, within the limits of analysis (approximately $\pm$ 0.01 %) showing that diffusion of carbon through the specimen was fast compared with the absorption of carbon from the atmosphere. Furthermore, the increase in carbon content at 1,000° C was slightly less than that at 900° C. Since reaction kinetics will be much faster at 1,000° C than at 900° C, this suggests that at 1,000° C the carbon content of the alloy was controlled by thermodynamic equilibrium with the environment. Thus no further increase in carbon level would be expected with longer exposure at this temperature.

These observations clearly support the suggestion that for many alloys the worst corrosion problems may not be met at the highest operating temperatures of components in advanced HTRs. Further evidence for this has been found on a thermocouple sheath that had been in service for about 14,000 hours in the core of the Dragon Reactor [26, 27]. This sheath was made from type 321 steel wound with Inconel 600 wire. The

part of this sheath that had been exposed to be highest temperature (about 1,100-1,280º C) was still shiny after service, and showed no evidence of surface reaction.

γ′ Strengthened Alloys. — Figure 1 also summarises the effect of temperature on surface scale formation in the γ′ strengthened alloys Nimonic 80A and 713LC. These alloys showed lower oxidation rates than the type 321 steel at temperatures up to about 900º C. However, up to the highest exposure temperature (900º C) there was no sign that the oxidation rates of these alloys had reached maxima.

Figure 4 shows typical examples of the microstructures of these two alloys after exposure at 800º C (1) and 900º C. The general pattern was for the formation of a relatively thin surface scale (2-4 μm at 800º C, 5-10 μm at 900º C). Sub-surface oxidation was heavy compared with that found in austenitic steels [25]. However, in the steels this oxidation occurred mainly at grain boundaries, whereas with the higher Al and Ti contents the penetrations were more uniformly distributed. The depths of oxide penetrations in Nimonic 80A and Alloy 713LC were similar and reasonably small after exposure at 800º C (15-20 μm, compared with maximum depths of penetrations in Alloy 800 exceeding 100 μm at 800º C [25]. After test at 900º C the oxide had penetrated about 40 μm below the surface of Nimonic 80A, but only up to 25 μm in Alloy 713LC.

Nimonic 80A at both 800 and 900º C showed particles and needles of oxide which may have nucleated homogeneously. There was some evidence, particularly apparent in figure 4*a* that preferential oxidation had occurred at grain boundaries in a recrystallised surface layer.

Alloy 713LC tested at both 800º and 900º C showed patchy oxidation as is often found in nickel base, γ′ strengthened alloys exposed in air. At 800º C the sub-surface oxide within the patches had formed as a uniform distribution of fine needles (fig. 4*c*). At 900º C, however, the morphology of the oxide was quite different (fig. 4*d*), with shallow penetrations from the surface and a nearly continuous layer about 15 μm below the surface. Very little oxide was observed beneath this inner layer. Both inner and outer layers were probably Al_2O_3.

Assuming an aluminium activity of 0.05 in a typical gas turbine blading alloy, oxidation of aluminium in the range of p_{O_2} estimated above ($10^{-24\pm3}$ atm, see above) only becomes thermodynamically unfavourable at 1,300-1,500º C, so these alloys must rely on protective films if they are to be used successfully in advanced HTRs operating at 800-1,000º C.

Figure 5 shows a specimen of Alloy M21Z that had been exposed for about 17,000 hours at 900º C. This alloy had oxidised in a manner similar to 713LC, but the patchiness was not evident in this case, and the mode of oxidation appears far from protective.

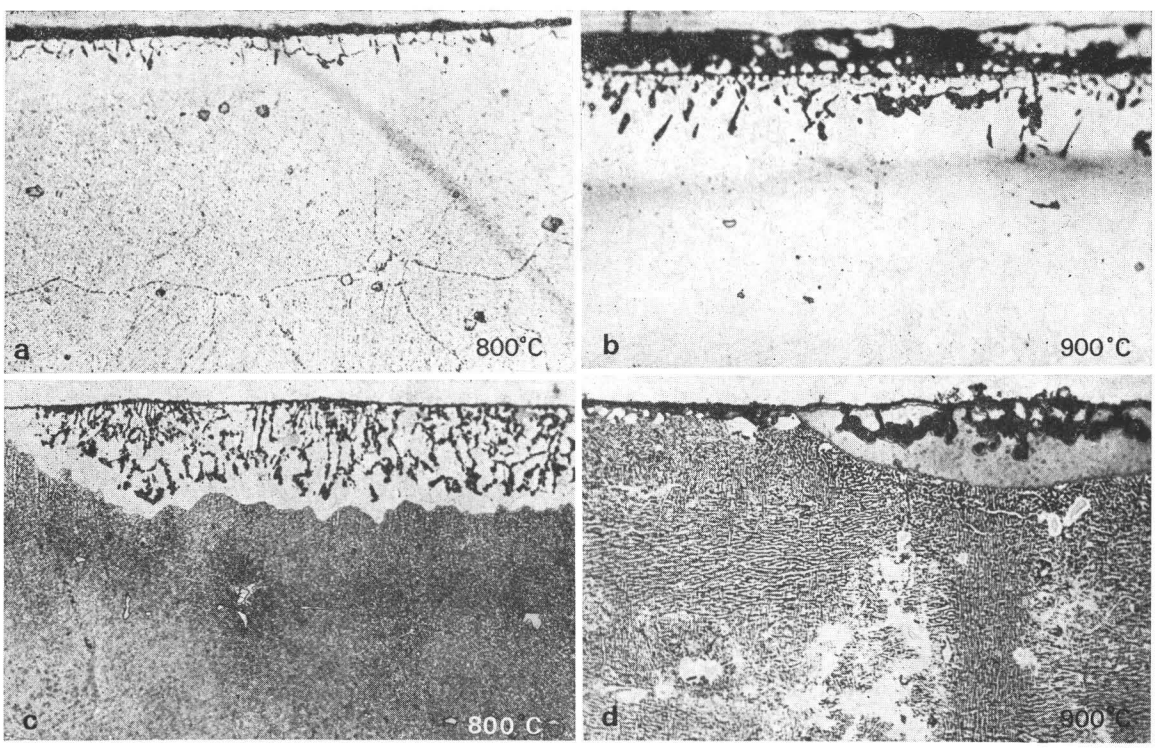


FIG. 4. — *γ′ Strengthened nickel base alloys exposed in HTR helium.* (a) *Nimonic 80A : 10,000 hours, 800º C ;* (b) *Nimonic 80A : 8,000 hours, 900º C ;* (c) *Alloy 713LC : 6,000 hours 800º C ;* (d) *Alloy 713LC : 5,000 hours, 900º C.*

(1) Specimens of Mimonic 80A were exposed at 800º C at different positions in the test furnace. Although the degree of corrosion varied from one specimen to another, the main features remained largely constant.

In summary, these observations indicate increasing surface oxide thickness with temperature up to at least 900° C in alloys that contain sufficient aluminium (or Al + Ti) to give γ' precipitation. However, the most striking effect of temperature, particularly in the alloys containing about 6 % Al, was on the morphology of the sub-surface oxide. The data so far are too few for detailed analysis, but they suggest that there is enough aluminium available close to the surface to prevent oxygen diffusing to a great depth. Clearly, however, the aluminium contents of alloys 713LC and M21Z are not sufficient for the formation of a totally protective film. The possibility that aluminium and titanium can interact beneficially is discussed below.

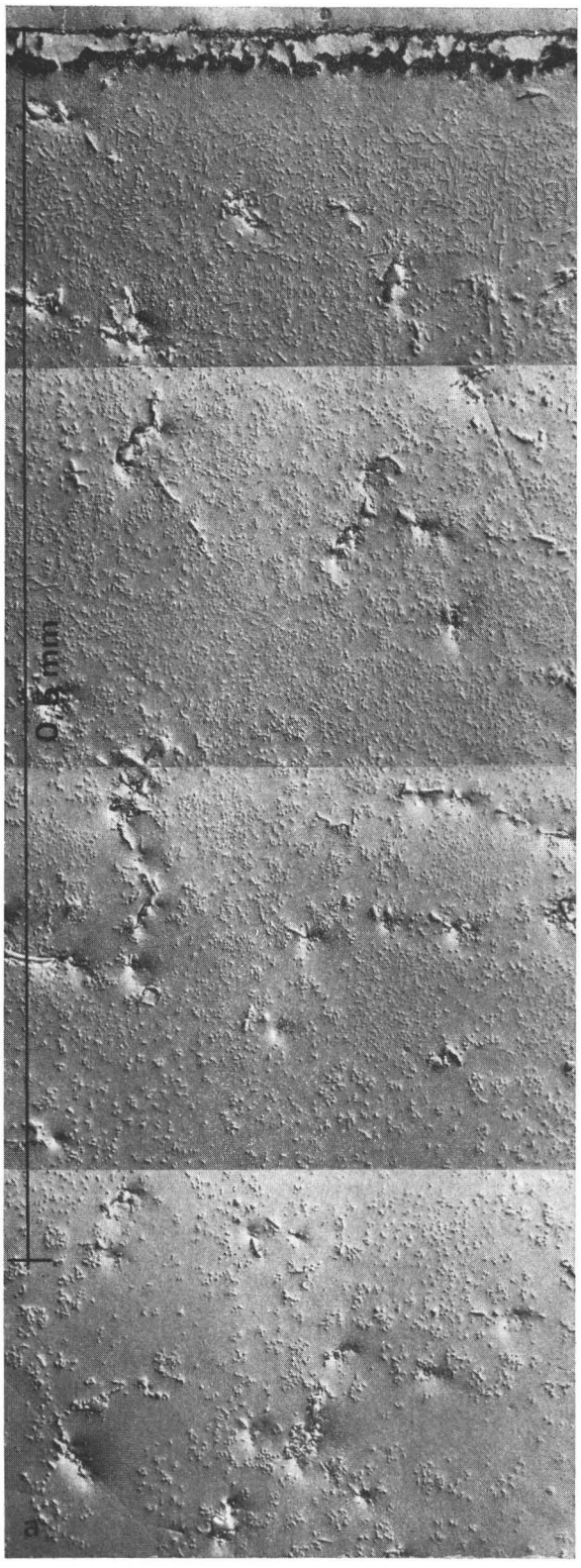


FIG. 5.

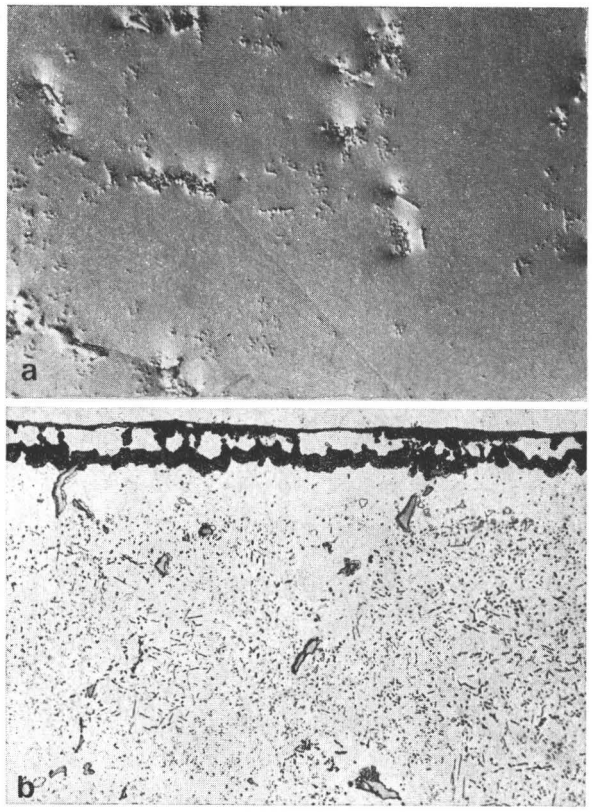


FIG. 5. — *Alloy M21Z exposed 1,700 hours at 900° C in HTR helium.* (a) *Unetched: use of Normaski illumination shows carburisation > 0.5 mm deep;* (b) *Etched: shows surface and sub-surface oxide layers.*

3.4. Effect of Alloy Composition on Oxidation and Carburisation Behaviour

Niobium and Titanium. — The influence of niobium and titanium on the corrosion behaviour of austenitic steels in HTR helium at temperatures up to 800° C has been discussed previously [25]. Essentially, steels containing less than about 20 % nickel which were stabilized with additions of 0.16 to 1.0 % niobium developed thin continuous oxide scales with no sign of sub-surface carburisation or intergranular oxidation. In contrast similar steels stabilised with up to 1 % titanium but no niobium showed relatively thick oxide films that were often accompanied by carburisation and intergranular oxidation below the surface. Alloy 800 with 30 % nickel, formed with oxide scales similar to those found on the niobium steels, but there was some intergranular oxidation of aluminium and titanium. Thus in the austenitic steels at temperatures up to 800° C small additions of niobium have a major beneficial effect on corrosion as do increases in nickel content.

Titanium and Aluminium in IN-102. — IN-102 contains typically 1 % (Al + Ti). However, in early Dragon work (Phase 1, atmosphere A) corrosion tests were done on a laboratory cast of « IN-102 » that contained less than 0.1 % each of aluminium and titanium [28]. Later tests in drier helium (atmosphere B) used a more representative commercial cast of alloy. The scale thicknesses on both casts are plotted in figure 1. The oxide on the commercial IN-102 is almost three times as thick as that on the laboratory alloy. Since more rapid oxidation would normally be expected in the wetter gas, differences in atmosphere cannot account for this observation so it appears to be due to the difference in aluminium and titanium contents. There was no significant difference between the depths of sub-surface oxidation in the two casts, but the penetrations were shallow in all cases ($\sim$ 10 μm at 750° C). Recent tests in helium at 700° C [29] have also shown that corrosion rates in Grade 2 Alloy 800 tended to increase with increasing levels of (Ti + Al) in the range 0.52 to 0.86 wt % but the data are only preliminary (2,000 hours).

These observations support earlier suggestions [25] that the corrosion resistance of an alloy in HTR helium depends on the levels of minor, reactive elements, as well as on the main alloy constituents. Elements that are normally used for deoxidation during melting, such as manganese, silicon, titanium and aluminium, may need particularly careful control if the corrosion resistance of an alloy in an HTR is to be optimised.

Cast Alloys for Gas Turbine Blades. — Metallographic observations in the high aluminium alloys 713LC and M21Z exposed at 800 and 900° C have been discussed above. Preliminary weight gain measurements are available for a wider range of cast, nickel base, blading alloys and these are summarised in figure 6. Further details are given elsewhere. The weight gains clearly fail into three groups at both 800 and 900° C.

The first group consists of the high aluminium, low chromium alloys M21, M21Z and IN-591. The oxidation behaviour of these will probably be similar to that of the M21Z discussed above and shown in figure 5, with considerable sub-surface oxide distributed uniformly over the specimen.

The second group consists of the related alloys 713LC and Mar M004 which have similar aluminium but higher chromium contents than the alloys in the first group. Again the oxidation behaviour should be as discussed above, with internal oxide present only in patches.

The third group consists of the titanium containing alloys IN-100 and IN-738, and shows a much lower weight gains than the other two groups. Furthermore, the majority of the weight gain has occurred in the first 1,000 hours of test, indicating the formation of a stable oxide scale with relatively little internal oxidation. These specimens have not been examined metallographically and so confirmation of this suggestion is not yet possible.

The differences suggest that, at these higher temperatures, the amount of internal oxidation is reduced by additions of either chromium or titanium to alloys containing 3-6 % aluminium. Explanations for this are not clear, but three possible mechanisms are given below:

a) The chromium and titanium may modify the chemistry of internal structure of the oxide scale.

b) The elements may influence the diffusivity of oxygen in the alloy, although this seems unlikely for titanium in the light of experience with the austenitic steels [25].

c) Perhaps the most likely mechanism, especially with titanium, is that the total content of elements that form highly stable oxides may be sufficient to limit oxidation to the surface, as discussed above.

An understanding of this effect clearly requires considerably more work. There is so far no data to show whether the oxidation behaviour of alloys of the M21 type will be seriously detrimental to mechanical properties. However, if oxidation of the higher titanium alloys is confirmed as being restricted to a surface scale, this behaviour should be preferred. The cobalt content of IN-100 may prevent its use in a direct cycle turbine linked to an HTR. Thus, there may be value in developing a cobalt free alloy which is in other respects similar to IN-100.

Molybdenum Alloy TZM. — Of the two casts of TZM tested so far, L1(*a*) the standard wrought alloy

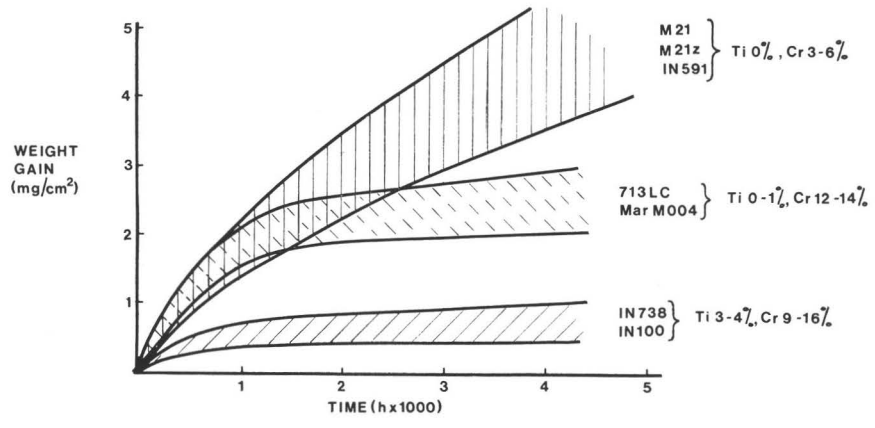
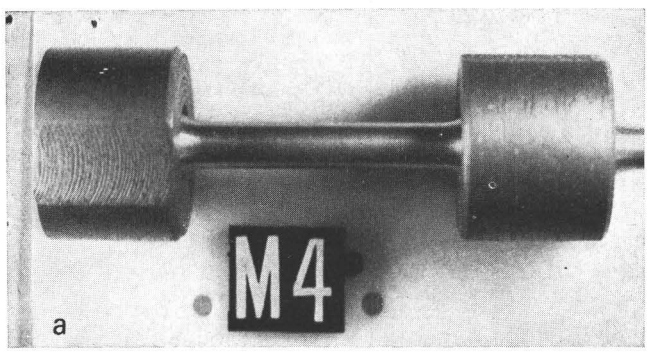


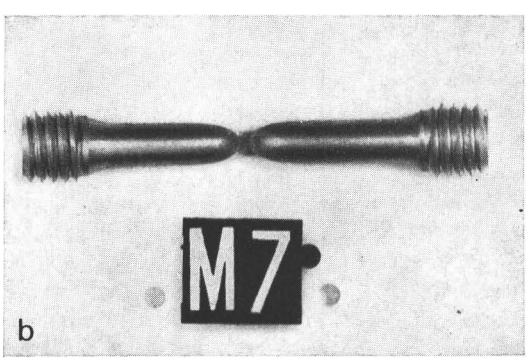
FIG. 6. — *Weight gain of cast high nickel alloys at 900° C.*

and L1(*c*) manufactured by the powder route, all specimens remained bright and unoxidised after testing at 900 and 1,000° C (fig. 7*a* and 7*b*). There was no evidence of any surface effects or change of structure and grain morphology in the interior of the specimens (fig. 7*b* and 7*c*).

3.5. **Effect of Environment on Creep Strength**

Work on austenitic steels [25] has shown that creep properties in helium were at least as good as those in air but the data available were insufficiently precise to allow a detailed appraisal of the effects of environmentally induced structural changes on creep strength. It was, however, clear that intergranular oxidation or sub-surface carburisation in AISI 316 and 12R72





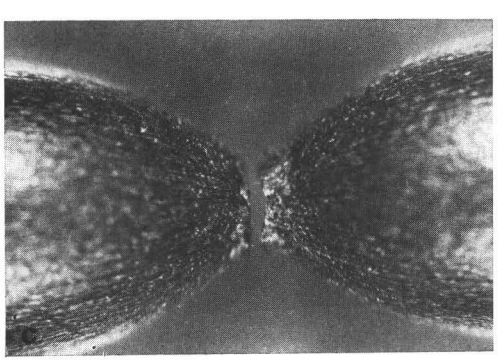


FIG. 7. — *TZM (L1(a)) after exposure at 900° C and 1,000° C.* (a) *Bright surface of specimen M4 (and TZM collets) after 2,000 hours at 1,000° C;* (b) *Specimen M20 exposed for 2,000 hours at 900° C showing no change in microstructure near the surface;* (c) *Localized grain deformation of specimen M7, ruptured after 830 hours at 900° C.*

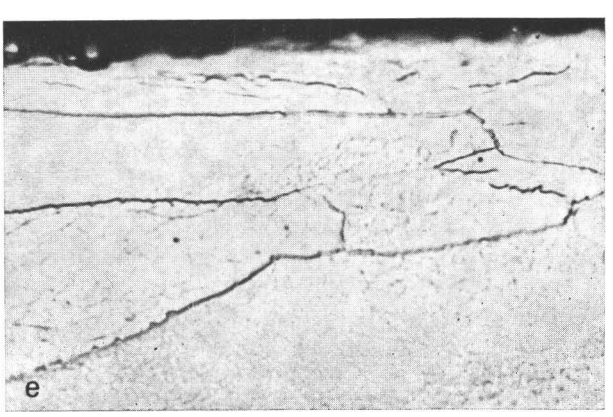


FIG. 7.

steels did not impair creep properties in helium relative to those in air. There was one important example of an effect of environment on creep of Grade 2 Alloy 800 at 650° C where testing in air assisted surface cracking and onset of tertiary creep but appeared to reduce crack propagation rate relative to helium.

The creep testing of the higher strength materials in the 800° C-1,000° C range has not yet reached 5,000 hours and it is, therefore, not possible at this stage to make an assessment of effects.

However, some indication of the type of the variable nature of the effects which might be expected are illustrated by some results on a limited range of materials tested between 750 and 850° C.

Hastelloy X. — Hitherto, creep tests in air for this alloy have not exceeded 5,000 hours but stress for given strain or rupture (fig. 8*a*) or stress for given creep rate (fig. 8*b*) were not significantly different in helium and air. There was no evidence of any effect of environment on the time to tertiary creep or on rupture ductility. The similarity in creep properties in the two atmospheres occurs in spite of certain structural differences. Carburisation occurred near the surface of helium tested specimens; typically this extended up to 100 μm after 10,000 hours at 750° C (fig. 9). Surface intergranular oxidation was also noted in helium (*e. g.* 20-40 μm after 10,000 hours exposure of a stress free sample). The conclusions for this material were therefore similar to those reported for AISI 316 and 12R72 steels at the same temperature [25]. They apply, however, only to relatively short test times.

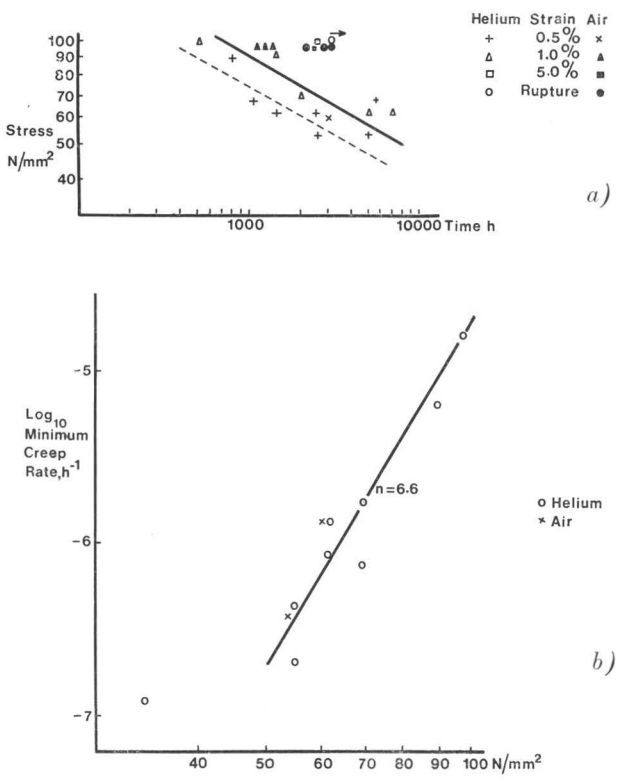


FIG. 8. — (a) *Stress/Log time plots for Hastelloy X at 750° C;* (b) *Minimum creep rates vs. stress for Hastelloy X at 750° C.*

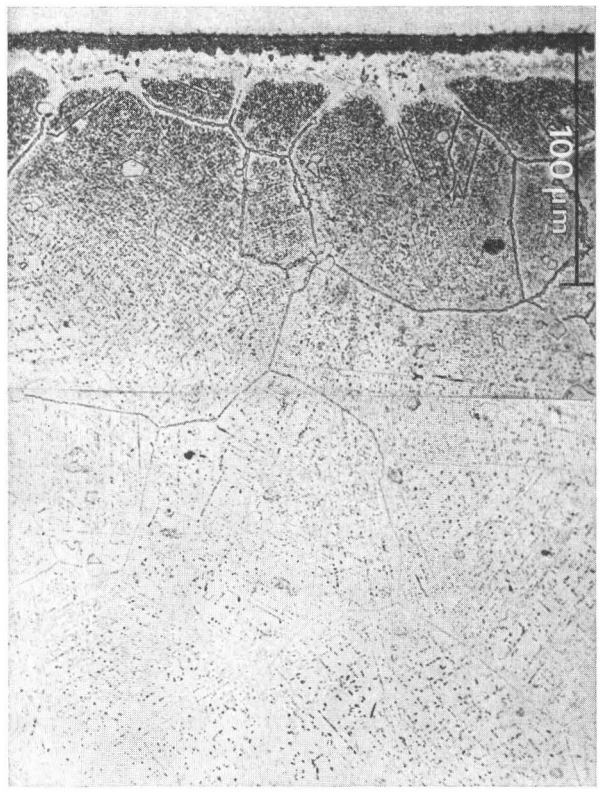


FIG. 9. — *Hastelloy X exposed 10,000 hours at 750° in HTR helium.*

Grade 1 Inconel 625. — Tests on this alloy at 750° C are summarised in table V. There was no evidence of any effect of environment on creep properties for tests up to 4,000 hours but slight indication that life in helium was longer than that in air at longer times (5,000 hours, 94 N/mm²). Ductility in both environments was high. Helium tested specimens showed only thin surface oxides (1-2 μm) with some intergranular oxidation in strained specimens, probably due to oxi-

TABLE V. — *Summary of Creep Results for Inconel 625 (Grade 1) tested in helium and air at 750° C.*

	Stress N/mm²	Test Duration hrs	Final Strain %	Comments
Helium	117	2,260	45	Terminated
	117	2,260	30	Terminated
	117	2,260	82	Ruptured
	105	2,500	10.7	Terminated for metallography
	105	3,500	28	Terminated
	105	3,500	36	Terminated
	94	2,500	4.2	Terminated for metallography
	94	4,500	27	Terminated
	94	5,265	135	Ruptured
Air	100	2,000	6.0	Terminated
	100	4,522	109	Ruptured
	100	4,000	92	Ruptured
	94	3,990	126	Ruptured
	94	4,750	103	Ruptured
	94	4,750	27	Terminated

dation in growing creep cracks. The alloy also showed formation of unidentified plate like precipitates, probably of a type discussed elsewhere [30]. There was no evidence for sub-surface carburisation from helium.

Grade 2 Inconel 625. — Creep data at 850° C, summarised in figure 10 and table VI, show that creep resistance in helium was substantially higher than that in air. Time to reach 2 % strain at given stress was 5 to 10 times greater in helium than air and stress for given strain and time was about 20 % greater in helium over the limited range where comparisons were available. Similar conclusions apply to a second somewhat weaker cast of this alloy which is now on test.

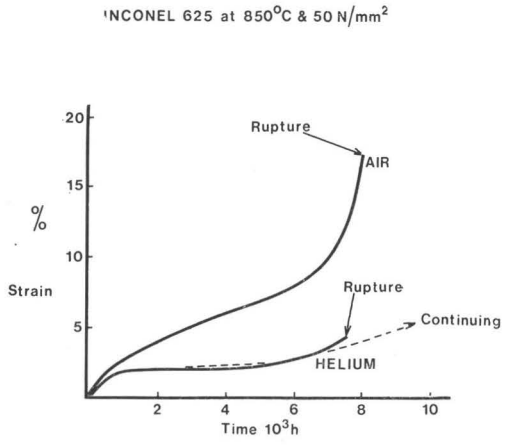


FIG. 10. — *Creep curves of Inconel 625 in helium and air at 850° C.*

TABLE VI. — *Summary of Creep Results for Inconel 625 (Grade 2) tested in helium and air at 850° C.*

	Stress N/mm²	Test Duration hrs	Final Strain %	Comments
Helium	58	3,000	3.6	Continuing
	58	3,000	4.1	Continuing
	50	7,755	4.5	Ruptured
	50	9,000	4.7	Continuing
	48.5	5,000	1.9	Terminated
	48.5	9,000	4.0	Continuing
	48.7	9,000	3.7	Continuing
	47.7	9,000	3.3	Continuing
	46.8	9,000	2.9	Continuing
Air	50.6	8,090	32	Ruptured
	50.1	8,070	18	Ruptured
	48.5	8,000	6.1	Terminated
	48.9	10,240	18	Ruptured
	47.1	10,480	10	Ruptured
	47.1	9,072	8.3	Ruptured

This strengthening did not seem to arise from obvious structural features in the alloy since, although some carburisation was noted in helium this was less than that seen in Hastelloy X after test at 750° C. Precipitation of several second phases was noted after test in both air and helium although the density of second phase was less than that in the same alloy tested in the Grade 1 condition at 750° C.

The difference in behaviour may however be associated with easier nucleation of creep cracks in air as was noted in Alloy 800 at 650° C [25]. This would account for many of the differences in shape of the creep curves of figure 10 (*e. g.* higher secondary creep rate and earlier tertiary in air). Metallographic examination of air tested specimens showed some surface cracking, typically 150 μm deep after about 8 % strain. Helium specimens tested to 2 % strain were free of surface cracks although there was some (15 μm) intergranular oxide penetration.

The single ruptured helium specimen (fig. 10) suggests further similarities in the behaviour of Alloy 800 at 650° C and Inconel 625 at 850° C. The shape of the creep curve of this specimen, which had virtually no tertiary creep stage, and its relatively low ductility suggest that crack propagation in Inconel 625 in helium may be much easier than that in air. This clearly warrants further study as it implies that creep cracks may develop and grow in helium with very little warning.

Inconel 617 at 850° C. — Creep tests on this alloy are summarised in table VII. At the higher of the stresses used at 850° C (42 N/mm²), there was a tendency for creep strength (*i. e.* stress for given strain in given time) in air to be slightly greater than that in helium but at the lower stress (37 N/mm) no difference could be discerned between the two atmospheres. No rupture data are available so far and comparisons apply only up to 6,000 hours.

TABLE VII. — *Summary of Creep Tests in helium and air for IN 617.*

	Temp. °C	Stress N/mm²	Duration hrs	Final Strain %	Comments
Helium	800	51.4	2,000	0.30	Continuing
	800	51.2	2,000	0.09	Continuing
	850	42.3	2,000	1.70	Terminated
	850	42.2	2,000	2.31	Continuing
	850	42.2	2,000	1.84	Continuing
	850	37.0	6,000	0.52	Continuing
	850	36.4	2,000	0.11	Terminated
	850	36.4	6,000	0.66	Continuing
	900	20.9	3,000	5.29	Terminated
	900	20.9	4,000	4.76	Continuing
Air	850	42.3	3,000	0.89	Continuing
	850	42.2	3,000	1.60	Continuing
	850	36.4	2,000	0.18	Terminated
	850	36.4	10,000	2.23	Continuing
	850	36.5	10,000	2.12	Continuing

Metallographically, it was noted that surface oxide depths after 2,000 hours were less in helium than in air (typically 1-2 μm and 8-10 μm respectively). Internal oxidation also occurred in both atmospheres (maximum depths in helium were about 20 μm compared with about 30 μm in air after similar time and strain). There was a tendency for the internal oxidation in helium to take the form of distinct penetrations which were not specifically associated with grain boundaries but were uniformly distributed with a spacing of 10-15 μm

on a longitudinal section. In air, oxide tended to occur as discrete particles in a zone beneath the outer oxide. So far, it has not been possible to recognise any significant carburisation from helium.

4. *CONCLUDING REMARKS*

The above summary of some of the recent developments in the Dragon metals work identifies several important areas for future study.

Corrosion studies on AISI 321 steel at 800 to 1,000º C have shown that the oxygen partial pressure in the equipment adjacent to materials with ~ 20 % Cr is as low as $10^{-24\pm3}$ atm which is similar to that expected during operation of an HTR. At these levels, nickel and iron cannot be oxidised above about 500 and 600º C respectively, chromium ceases to oxidise at 800 to 900º C and titanium at 900 to 1,000º C, depending to some extent on alloy composition. Aluminium, however, will be oxidised up to 1,300-1,500º C so satisfactory behaviour of γ' strengthened superalloys in advanced HTRs operating at 800-1,000º C must depend on establishment of a protective corrosion mechanism rather than on thermodynamically induced immunity to attack. Preliminary weight gain data, which can often be usefully correlated with observed corrosion depths, have suggested that those protective mechanisms are assisted by the presence of titanium and possibly chromium in superalloys.

Carburisation, reported earlier in austenitic steels, has again been identified metallographically in several high temperature materials, *e. g.* Hastelloy X and M21Z. So far it has not been possible to classify carburisation behaviour in terms of alloy composition but the carbon analysis of machined layers is likely to prove of benefit in this.

Up to limited test periods, the Molybdenum Alloy TZM appears to be completely inert in HTR helium at 900º C and 1,000º C.

Both oxidation and carburisation might be expected to affect mechanical properties but the only effect noted so far is the tendency now noted in two alloys (Alloy 800 and Inconel 625) for HTR helium to suppress surface crack initiation but to accelerate crack propagation rate to an extent which may seriously limit ductility in tertiary creep. This requires further study, especially as it simplies that fatigue crack growth or crack growth from pre-existing flaws in a structure may prove much easier in helium than would be excepted from air tests. There were alloys, however, where this accelerated crack growth was not apparent, *e. g.* AISI 316 steel [25], Hastelloy X or fine grained Inconel 625 at 750º C. Clearly, one of the aims of present and future work should be to identify factors causing susceptibility to rapid crack growth in helium, as well as materials immune to this.

Crack growth rate measurements would be of value but, as shown above, rupture testing in helium and air can provide a useful indication of an alloy's likely behaviour as well as allowing the testing of many more materials than would normally be covered in a programme of measurements of crack growth rates.

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ACKNOWLEDGMENT. — In compiling this Report the author has relied heavily on the work of his colleagues in the *Dragon Metals Team*. Especial thanks are due to H. G. A. BATES, K. BRENNER, R. R. COOK, D. F. LUPTON, M. R. WARREN and F. WADE.

Also the loyalty to the work in difficult times of the teams at *CIIR*, Oslo and *OSGAE*, Seibersdorf is gratefully acknowledged.

Finally, the author would like to specially thank Mr. R. A. U. HUDDLE. It should be noted that without his foresight and enthusiasm this work would not have been initiated and developed.

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 204-211

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HIGH TEMPERATURE MATERIALS REQUIREMENTS IN REFORMING OF GASEOUS HYDROCARBONS WITH HTR HEAT

By

H. F. NIESSEN, K. KUGELER and M. KUGELER

1. *INTRODUCTION*

Nuclear Process Heat is a new source of primary energy together with natural gas, oil and coal. In the gasification of coal large amounts of nuclear energy can be transferred into chemically bound energy in the form of substitute natural gas (SNG) or synthesis gas [1, 2, 3]. Another very interesting process is the Chemical Heat Pipe (Adam-Eva), where the nuclear heat is also transferred into chemically bound energy and brought by cold-gas transport to the consumer. Here energy is released by the reverse reaction [4]. Typical for Nuclear Process Heat is a High-Temperature Reactor with a helium outlet temperature of 950° C. The hot helium is led via hot gas ducts to Process Heat Exchangers (PHX), where on the secondary side a chemical reaction takes place. The core of a HTR with graphite fuel elements and ceramic structures (graphite, carbon stone) has the capability to deliver nuclear heat at very high temperatures. This could be demonstrated by the operation of the AVR (15 MWe pebble bed reactor) with a mean helium outlet temperature of 950° C since nearly 2 years [5]. Nevertheless work is still required to improve the fuel elements (coated particles) and the reflector graphite. A lot of serious questions have arisen concerning metallic materials for the different components outside the core especially the PHX.

Based on the promising results of the development of the last few years, in FRG a new project has been started a few month ago. The aim of this project (PNP) is the development, design and construction of a nuclear process heat prototype plant for coal gasification. In the following the helium-heated steam reformer will be discussed as a typical example for a process heat exchanger.

2. APPLICATIONS OF STEAM REFORMERS

The steam reformer is used to convert all the different sorts of light hydrocarbons such as natural gas, methane or naphtha with steam to hydrogen or a mixture of hydrogen and carbon monoxide. Steam reforming is an endothermic catalytic process with a large demand of heat at temperatures in the range of 700-850° C and a pressure of upto 40 bar in conventional plants. The gas analysis is dependent on temperature, pressure and the steam/hydrocarbon ratio. There are two main reactions in the steam-reforming process.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad \Delta H = \quad 205.2 \text{ kJ/mole}$$
$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \Delta H = - \quad 41.9 \text{ kJ/mole}$$

The product gas of steam reforming is then fed into different processes (fig. 1). Typical fields of applications are:

1. Hydrogasification of either bituminous or lignite coals.
2. Chemical Heat Pipe, to transport nuclear energy over long distances. The steam reforming process is connected with a methanation process situated near

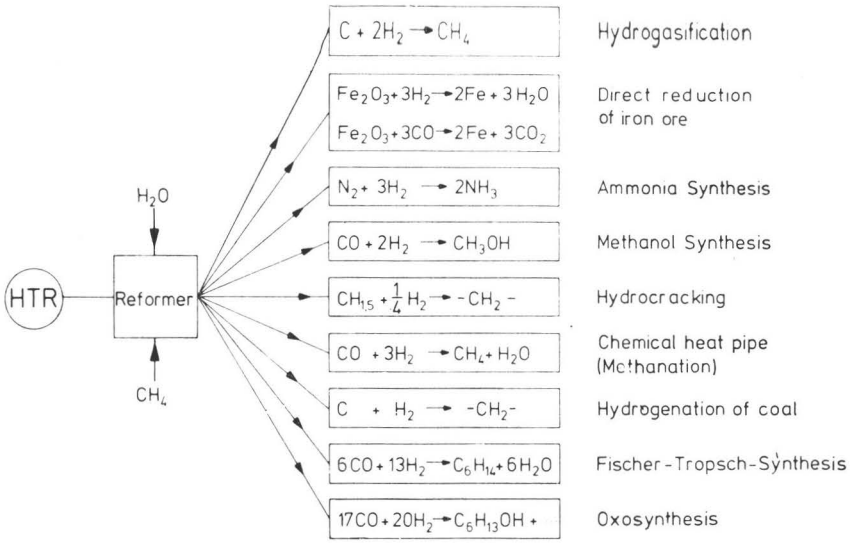

FIG. 1. — *Application of steam reformers.*

the consumers, where the reverse reaction takes place and heat is set free.

3. Direct reduction of iron ore.

4. Production of synthesis gas for methanol synthesis, oxosynthesis and Fischer Tropsch-synthesis.

5. Production of hydrogen for ammonia synthesis, hydrocracking of heavy fuel oils into light hydrocarbons or hydrogenation of coal to convert coal to gasoline.

3. REQUIREMENTS FOR THE TUBE MATERIAL

To get a better overview in this chapter not only the requirements for helium-heated reformer tube materials are shown, but also a comparison to the conventional techniques is given.

3.1. Temperatures, Heat Transfer and Heat Fluxes

The differences in the requirements are based on the different kind of heating. While on the process side the parameters are similar for the conventional and the nuclear process, very different parameters are on the heating side. The energy supply to conventional steam reforming plant is based on the burning of light hydrocarbons. The fuel is burned with preheated air in burners located at the top and the side of the furnace. The combustion gas (flame temperature $\approx$ 1,500º C) flows downwards in parallel with the flow of the process gas. The feed gas flows downwards through the catalyst-filled tubes ($\approx$ 10 m long) and is converted by the reforming reaction. A schematic flow sheet of the conventional process is shown in figure 2. In the upper section of the tube, the heat flux is very high because of the large temperature difference. In utilizing nuclear reactor heat the maximum temperature of the heat source is about 950º C. An economical reformer design in a nuclear process must also achieve a high heat flux. Because of the counterflow arrangement and the excellent heat transfer properties of helium at high pressure, such a high heat flux can be achieved. In this case the lower temperature difference is compensated for by the high heat transfer coefficient on the heating side. The numbers shown in table I are typical for the process and illustrate the comparison between the nuclear and the conventional process. The values for the helium-heated steam reformer have been verified in the pilot plant Eva at the KFA Jülich, utilizing a single original-sized tube [4]. In figure 3 a comparison of the temperature and heat flux profiles for the nuclear and the conventional process is shown. A certain disadvantage of the conventional heating is the non-uniform heat flux around the circumference of the tube. There is an azimutal variation of the heat flux of $\approx$ 30 %.

TABLE I. — *Heat transfer of nuclear and conventionally-heated steam reformer process.*

	Nuclear Process	Conventional Process
Heat transfer coefficient on the process side	1,200 W/(m² ºC)	1,200 W/(m² ºC)
Heat transfer coefficient on the heating side	830 W/(m² ºC)	170 W/(m² ºC)
Overall heat transfer coefficient . . .	340 W/(m² ºC)	130 W/(m² ºC)
Mean heat flux. .	64,500 W/m²	65,000 W/m²

In table II the typical temperatures are summarized. From all this follows:

— *The maximum helium temperature of 950º C is sufficiently high to obtain a heat flux for the nuclear process as high as for the conventional process.*

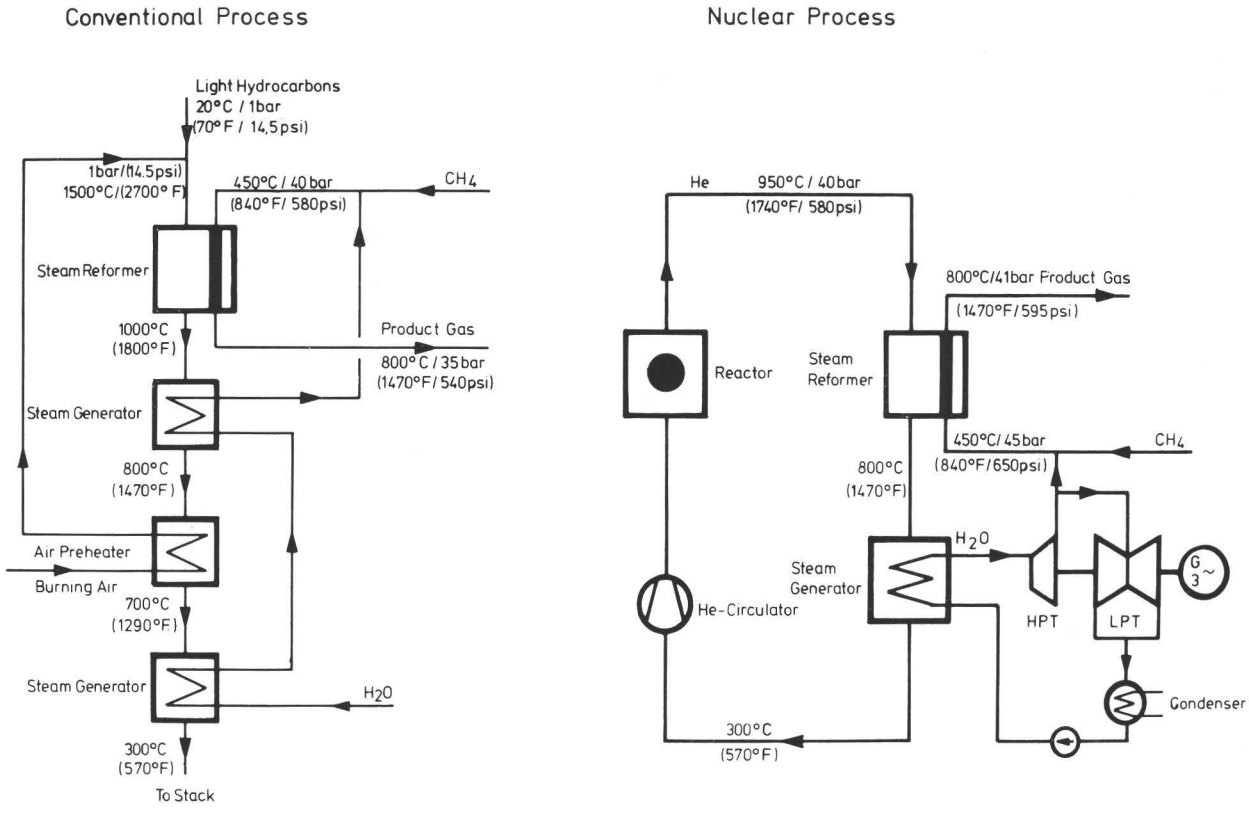

FIG. 2. — *Flow scheme for the nuclear and conventional steam reformer.*

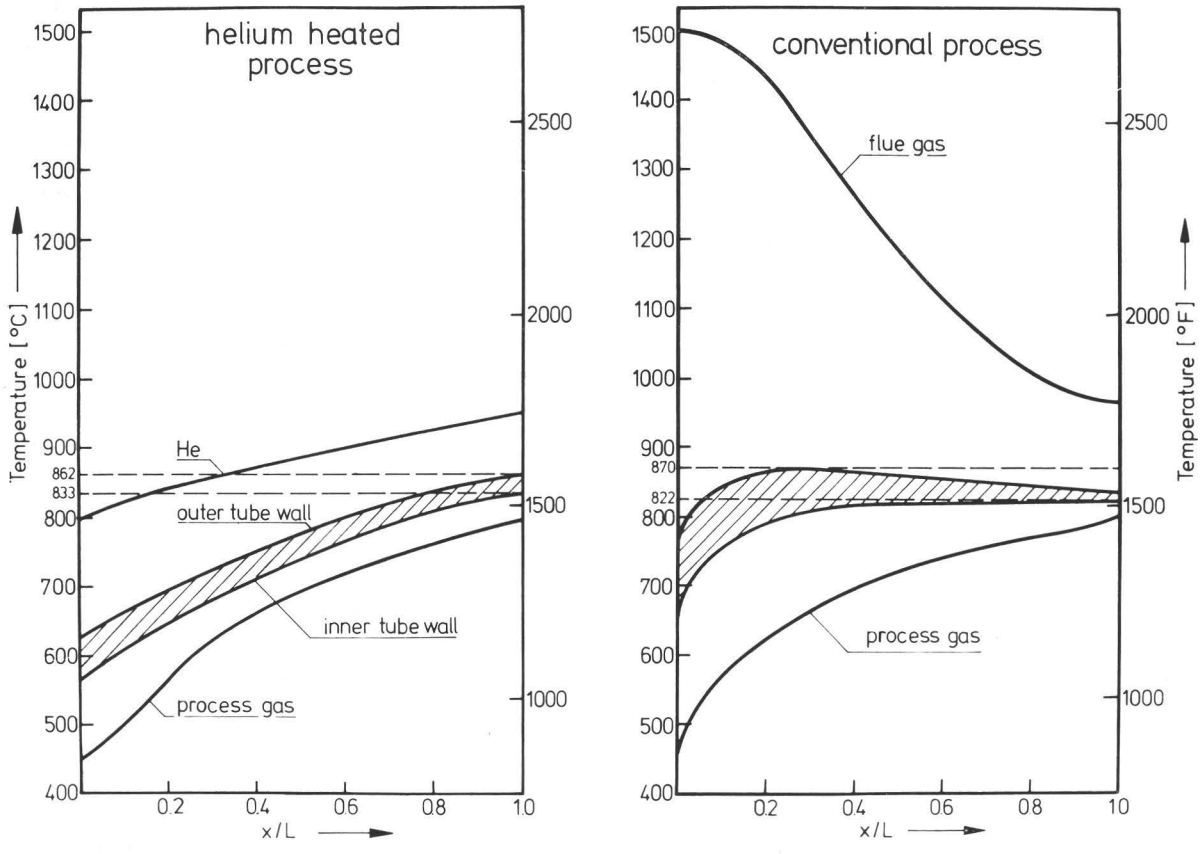

FIG. 3 (a). — *Temperature profiles.*

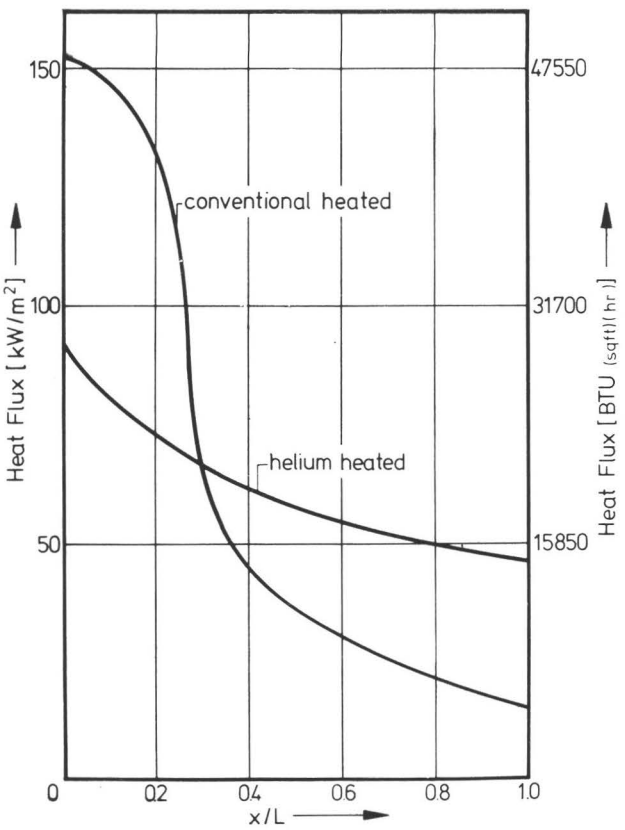

FIG. 3 (b). — *Comparison of heat flux.*

TABLE II. — *Temperatures and heat flux at normal operation.*

	Nuclear	Conventional
Max. wall temperature outside.	862° C (1,585° F)	870° C (1,600° F)
Max. wall temperature inside.	833° C (1,530° F)	822° C (1,510° F)
Min. wall temperature outside.	630° C (1,165° F)	750° C (1,380° F)
Temperature difference at max. wall temperature. . . .	29° C (55° F)	75° C (138° F)
Max. heat flux.	92 kW/m²	150 kW/m² (± 15 %)
Min. heat flux.	47 kW/m²	15 kW/m² (± 15 %)

— Because of the maximum helium temperature of 950° C, no wall temperature greater than 950° C is possible.

— The heating for the nuclear process is more uniform and causes therefore smaller temperature differences.

3.2. Stresses in the Steam Reformer Tubes

3.2.1. **Normal Steady-State Operation.** — During normal operation, the primary stresses in the tubes are caused by pressure difference. The helium pressure in the primary circuit of about 40 bar results from thermodynamic and economical optimization considerations. The pressure on the process side is selected slightly higher than the helium pressure to prevent primary helium entering the secondary process in case of tube rupture *e. g.* coal gasification. For a thick-walled tube with the typical dimensions (length = 10 m (33 ft) OD = 130 mm (5.1 in), ID = 100 mm (4.3 in)), the stresses can be calculated with: η = OD/ID, $\Delta p = p_i - p_{out}$ and the compound stress after theory of maximum distortion energy

$$\sigma_{com} = \sqrt{0{,}5((\sigma_r - \sigma_t)^2 + (\sigma_r - \sigma_a)^2 + (\sigma_t - \sigma_a)^2)}$$

r = radial, a = axial, t = tangential, i = inside, o = outside.

	Wall inside	Wall outside
Tangential stress. .	$-p_i + \frac{2\eta^2}{\eta^2-1}\cdot\Delta p$	$-p_i + \frac{\eta^2+1}{\eta^2-1}\cdot\Delta p$
Axial stress . . .	$-p_i + \frac{\eta^2}{\eta^2-1}\cdot\Delta p$	$-p_i + \frac{\eta^2-1}{\eta^2-1}\cdot\Delta p$
Radial stress. . .	$-p_i$	$-p_i + \Delta p$
Compound stress .	$\sqrt{3}\cdot\frac{\eta^2}{\eta^2-1}\cdot\Delta p$	$\sqrt{3}\cdot\frac{1}{\eta^2-1}\cdot\Delta p$

For the helium-heated tube, the inside pressure goes down from 45 bar at the inlet to 41 bar at the outlet. In the following it is assumed that the inside pressure is 42 bar because of the relatively high pressure drop at the tube end. On the helium side the pressure is 39 bar. For the conventional tube the inlet pressure of 40 bar is assumed to be the inside pressure in the region of the highest wall temperature. The outside pressure is 1 bar. The resulting stresses are shown in table III.

TABLE III. — *Stress requirements for steam reformers.*

	Nuclear		Conventional	
	inside	outside	inside	outside
Tangential stress N/mm²	− 2.7	− 3.0	+ 15.1	+ 11.2
Axial stress N/mm²	− 3.5	− 3.5	+ 5.6	+ 5.6
Radial stress N/mm²	− 4.2	− 3.9	− 4.0	− 0.1
Compound stress	1.3 N/mm² (185 psi)	0.8 N/mm² (117 psi)	16.5 N/mm² (2,400 psi)	9.8 N/mm² (1,420 psi)
Maximum wall Temperature	833° C (1,530° F)	862° C (1,585° F)	822° C (1,510° F)	870° C (1,600° F)

+ ≙ tensile stress; − ≙ compressive stress.

All stresses for the nuclear-heated tubes are compressive ones i. e. *a spontaneous crack propagation is impossible.*

The compound stresses for the nuclear-heated tubes are 12 times less than those for the conventional heated tubes.

In figure 4 the 100,000 hours rupture strentgh of various materials and the stresses for the tube is shown.

From figure 4 follows:

There is a safety factor of 15 for the nuclear-heated tube against 100,000 hours rupture strength of the relatively simple materials HK40 and Incoloy 802.

From the standpoint of strength there is no necessity to introduce high strength alloys like oxide dispersion strengthened materials or Mo-TZM.

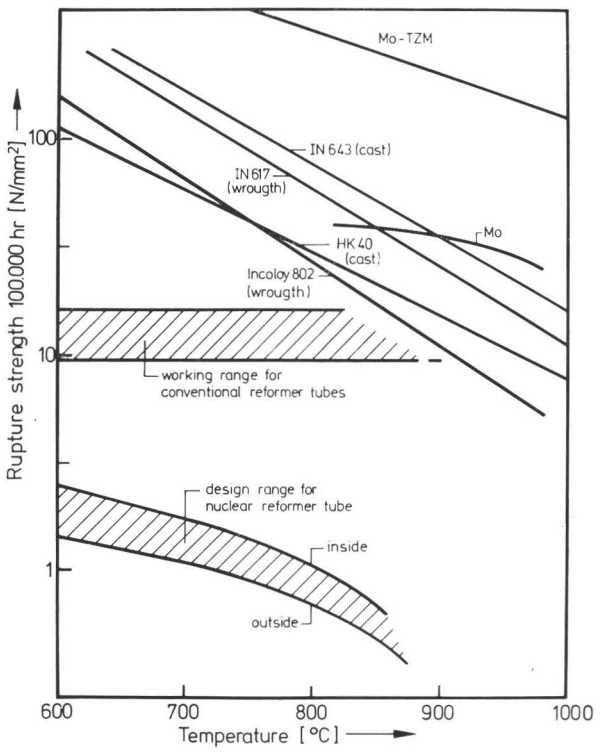

FIG. 4. — *Rupture strength and stress requirements.*

The thermal stress caused by steady-state temperature difference across the tube walls is relieved by creep and *e. g.* after 10 hours reduced to half of that at the beginning dependent on material data and temperature. However, this costs life-time. But the service time for HK40 calculated from these conditions would be greater than the life-time of the reactor plant if the extrapolation of material data to such long times would be allowable. Calculations for these conditions and HK40 give for 250,000 hours a rupture/damage-fraction of 0.25-0.35 dependent what data are selected (lower limit, average, or upper limit of the scattering band).

3.2.2. **Stresses caused by Start-Up, Shut-Down and Control.** — The starting and shut-down operation of the steam reformer has to be done sufficiently slowly in order to avoid thermo-shock. For a rate of temperature change ϑ_T, the stress occurring can be given approximately for elastic material [7].

$$\sigma_T = \frac{E \cdot \alpha}{1 - \mu} \frac{C_p \cdot \rho}{3 \cdot K} \cdot \frac{(OD - ID)^2}{4} \cdot \left(\frac{OD}{ID} \cdot 0.43 + 0.57\right) \cdot \vartheta_T$$

For a HTR the temperature change is limited to 100° C/hour because of the stresses in ceramic structures. As shown in figure 5 this value of 100° C/hour results in a stress of 1.3 N/mm² (≙ 0.2 ksi), *i. e.* the steam reformer is not the determining component.

The power control of a High-Temperature Reactor is achieved by changing helium mass flow in contrast to the conventional steam reformers where the power control is done by temperature change on the heating side.

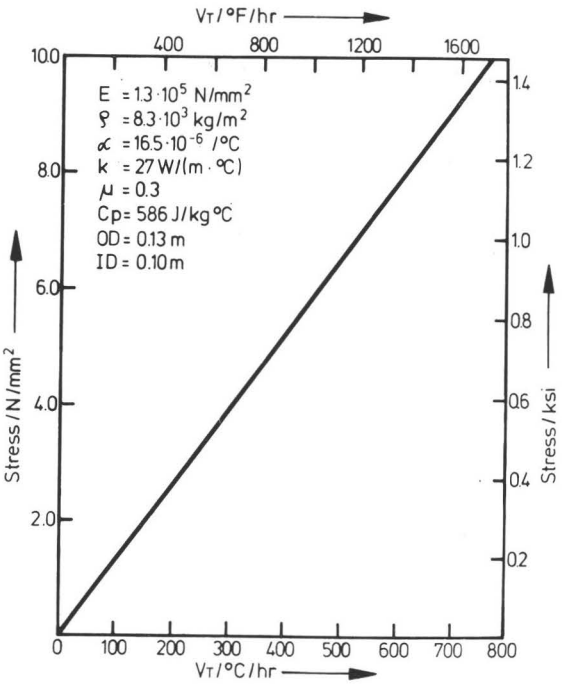

FIG. 5. — *Stresses caused by temperature change velocity.*

Short-time stresses caused by start-up or normal shut-down are small because the temperature change velocity is limited by ceramics in the core and the insulations in the furnaces.

For power control in the nuclear-heated steam reformer the temperatures are nearly unaltered.

The heating of the nuclear-heated steam reformer is very uniform and there is no temperature fluctuation as it is caused by flame heating.

3.2.3. **Emergency Case.** — The worst case for the reformer tubes is the break-down of feed supply. This accident is very umprobable for the nuclear heating because of the redundancy of the feed-water pumps but can, however, happen. In this case the material temperature would be raised to 950° C and the pressure difference across the tube walls would rise to 40 bar. In this case a stress of 17 N/mm² occurs for a short time. The buckling of the tube under outside pressure

is no problem. V. Mises has shown that the critical pressure is

$$p_{crit} = \frac{E}{12(1-\mu)} \cdot \left(\frac{OD - ID}{OD + ID} \cdot 2\right)^3 = 6\,230 \text{ bar}$$

For the conventionally heated reformer tubes this accident results quickly in wall temperatures of 1,200° C and more, *i. e.* the burners have to be stopped rapidly. However, a great temperature rise will occur because of the heat capacity of the bricks.

Another accident for the helium-heated reformer tubes is the loss of pressure on the helium side. This is the greatest design accident for the reactor plant but not for the steam reformer tubes. Because now the tube temperature decreases and the greatest problem is to limit the cooling velocity to a permissible rate. Summarizing it can be said that the break-down of the feed supply causes:

For the nuclear-heated tubes a maximum temperature of 950° C and a stress of 17 N/mm² (2.5 ksi).

For the conventionally-heated tubes a temperature rise to 1,200° C or more.

For the nuclear-heated tubes a life-time reduction of about 5,000-10,000 hours/per emergency case.

For the conventionally-heated tube a possible destruction.

3.3. **Hydrogen and Tritium Permeation**

A new problem for reformer tubes is the permeation of hydrogen from the secondary circuit to the primary helium. While in the conventional process the hydrogen permeation is no problem, this is a problem for the nuclear case, because of the corrosion of graphite in the reactor core. Therefore the hydrogen permeation has to be limited. While hydrogen diffuses very rapidly through bright metallic walls, experiments with mixtures of hydrogen and steam show that the permeation rate is inhibited by stable oxide layers if the process gas is oxidizing (see fig. 6 [9]). Oxidizing conditions are given on the process side because of the hydrogen/steam. Calculations give a hydrogen permeation of ≈ 0.3 Nm³/hour ($\hat{=}$ 11 Scuft/hour), which is a tolerable rate. Measurements of Mori *et al.* [10] indicate that for Ni based alloys (Inconel 600) the permeation rate for hydrogen is greater than for Fe based alloys (Incoloy 800) Another indication of this tendency is given in [11]. There is the catalytic effectiveness of Inconel 601 and Incoloy 800 shown and a quite similar tendency shown. This effect has to be studied carefully.

Another problem is the tritium permeation from the helium to the product gas. In a 3,000 MWth reactor plant $\sim$ 8 Ci/d released are to the helium. Under the very pessimistic assumption that all tritium in the helium is released to the product gas, the tritium concentration in the product gas (SNG) would be smaller than the allowed value for breathing air by a factor 3.5. But most of the tritium is removed in the helium purification system and this purification system has a very great effectiveness in the case of inhibited permeation. Then the tritium amount in the product gas is reduced by a factor $>$ 10,000.

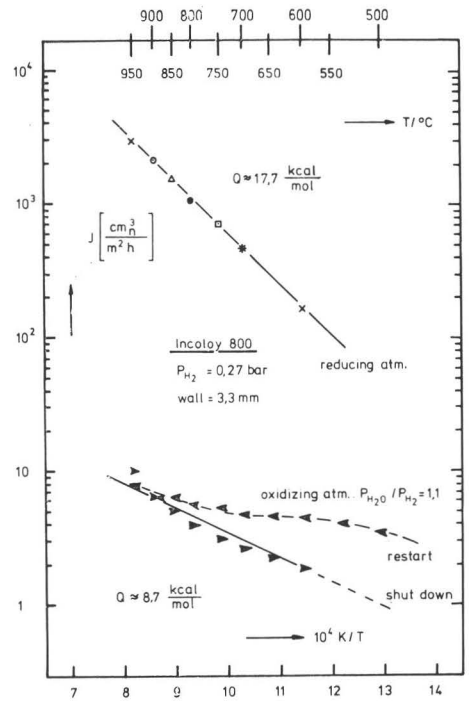

FIG. 6. — *H_2-Permeation vs. 1/T for clean and oxidized surfaces* [9].

The hydrogen and tritium permeation are tolerable if oxide layers are formed.

There is no necessity for an IHX from the standpoint of tritium permeation.

There might be a handicap for some of the proposed superalloys because of their greater hydrogen- (and tritium) permeation.

3.4. **Corrosion of Tube Materials**

From the standpoint of corrosion, the steam reformer directly heated by the primary HTR-helium, is an interesting component. There are two corrosion effects:

a) Corrosion by impurities of HTR-helium (H_2, CO, CO_2, H_2O) on the heating side.

b) Corrosion by process gas on the process side.

While on the helium side a reducing atmosphere exists, it is oxidizing on the process side. At first sight this appears to be especially complicated. But the temperatures of the walls are less than 900° C. As shown by Huddle [12, 13] for the helium side and by Kalwa and v. Heek [14] for process side, the phenomena are quite similar:

Al- and Ti- distribution in the alloy are strongly effected and the resulting alumina, for example, separates at the grain boundary.

The oxide layer consists of chromium, manganese, silicon, aluminium and titanium.

Silicon and carbon favour the oxidation of grain boundaries.

For strengthening and stabilizing, niobium should be used instead of titanium.

The alloys developed for the conventionally heated furnaces in petrochemical industries have an excellent

resistance to oxidation and carburization during reforming reactions for temperatures less than 1,000º C [15]. In the KFA a steam reformer tube from the Eva loop with an operation time of 2,400 hours was examinated. This tube showed no indication of corrosion [16].

4. Requirements for a development program

For the development of steam reformers heated by helium are necessary:

1. basic studies to establish the process *e. g.* thermodynamic reaction kinetics,
2. basic tests especially material tests,
3. design of the steam reformer,
4. material qualification,
5. test of modules of the selected design in a test facility,
6. construction and operation of a steam reformer in a nuclear reactor plant.

A part of this work has already started. The material program for the *German PNP-Project* is on the critical path. Typical questions from the design engineers are:

1. What is the long time strength of the materials (normal operation)?
2. Are the material properties measured under tensile stress adaptable for compressive stresses?
3. What properties can be utilized for short-time stresses after aging the material (emergency case)?
4. What are the data for the properties characterizing the stress relief (work hardening, elastic plastic calculations, low cycle fatigue)?
5. What is the hydrogen- and tritium-permeation rate under service conditions?
6. What is the volume increase caused by corrosion (eventually additional stress)?

All these data are necessary to come to the evaluation of a stress history for the steam reformer over the whole service time. Another complex of questions is related to the extrapolation of data:

1. How suitable are the strength data measured at higher stress or higher temperature for an extrapolation to operation conditions and service time (Larson-Miller)?
2. What extrapolation method is allowed for the corrosion? Are the data measured without stress, or at higher stress, or at higher temperature than operation conditions suitable?

A third complex in a development program is related to the quality assurance and control. Typical features are:

1. Improvement of fabrication technology to bring the product to a nuclear standard.

a) fabrication methods to get a more uniform product especially for centrifugal casting,
b) welding techniques,
c) fabrication of longer tubes to avoid weldings (for centrifugal casting but also wrought material).

2. Improvement or adaptation of non-destructive test methods (ultrasonic, magnetic methods) to the high-temperature material for new tubes and for repeat examination of tubes in service.

The fourth complex of questions is related to the development of internationally accepted codes.

Extension of ASME code case 1592 to higher temperature regions.

All these activities have to be done to come to an optimum design accepted by licensing authorities. This will be an iterative process and requires a good cooperation of metallurgy and design. The design has to start with very conservative assumptions and the component has to be replacable. At the time where more data are available a redesign will be necessary. It might be necessary that some of the long-time tests are carried out at a time where the prototype reactor is not only under construction but also in operation. With these new data the service time could be extended.

*
* *

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METALLURGICAL PROBLEMS OF THE HE—TO—HE HEAT EXCHANGER FOR ADVANCED HTR'S

By

R. A. U. HUDDLE (*) and H. W. FRICKER (**)

1. *INTRODUCTION*

At the present time a very large sum of « public money » is being spent on feasibility studies to assess the possibilities of utilising nuclear energy as an alternative heat source for what is generally known as « process heat ». In particular, attention is being directed to problems associated with coal gasification, steam/methane reforming, etc., processes which require temperatures in the range 750-900° C if they are to have a reasonable efficiency. Although the core materials and design of the HTR have been developed to the stage where the feasibility of core outlet temperatures of 950-1,000° C is proven, work on the development of constructional materials and primary circuit design has not kept pace, and one is now faced with the urgent problem of « catching up with the fuel », which at the present time has a capability of at least 200° C higher than the metals and alloys presently available for ducts, liners, valves, heat exchangers, etc.

During an assessment study carried out by one of the authors as part of the Dragon Project programme, concerning the coupling of a « Very High Temperature Reactor » — VHTR — with a conventional reformer, it became apparent that on both technical and safety grounds an intermediate heat exchanger might become necessary [1]. Furthermore it was clear that the metallurgical requirements for such a heat-exchanger would be very difficult to meet, as it would involve a plant of some 3,000 MW (th) operating on one side with HTR helium at a pressure of 40-70 bars and at a temperature in the range 900-1,000° C.

During the course of the Nuclear Process Heat — NPH — studies it is inevitable that one will experience much optimism and much pessimism. This uncertainty is quite normal when one is operating in an unfamiliar field; however, it is absolutely vital that every care should be taken to avoid the sort of reasoning that argues that days are longer in summer because things expand when they get warmer!

Ideally one would like to prove, rather than to assume that the intermediate heat exchanger is unnecessary, but at the present time, and with our present knowledge it would be unwise to proceed on this basis. In this paper an attempt is made to assess the need for such a heat exchanger, to indicate the nature of the problems involved, and to discuss the metallurgical problems to be studied if appropriate alloys are to be developed.

2. WHY AN INTERMEDIATE HEAT EXCHANGER ?

If it were possible to design, construct and operate the chemical side of an NPH plant, (*e. g.* a steam/methane reformer) heated directly by the primary cir-

cuit HTR helium, and to give the necessary guarantees regarding reliability and safety to both the operator and to the licensing authorities there would be no need for an intermediate heat exchanger. However, experience with such high temperature chemical plant gives little confidence that such guarantees can be given at this time, and one must therefore consider the means necessary to satisfy the safety requirements now demanded of all nuclear and associated plant.

It is important to appreciate from the outset some fundamental differences of design philosophy that exist between the nuclear and the chemical industries. These are primarily associated with radiation, fission products and induced activity, the effects of which in turn influence design philosophy. For example, with a direct cycle, the standards of reliability presently accepted for a conventional reforming plant would appear to be insufficient for the nuclear side as the increased cost of maintenance due to the activity of the primary circuit would be prohibitive. Furthermore, since contamination of the reactor primary circuit by process gases and of the process gases by fission products must be limited, the designer and metallurgist are faced with a problem exercising their ingenuity and skill to the limit.

Let us first consider the influence of contamination of the primary circuit coolant by process gases. Unlike conventional fossil fuelled plants which operate with excess oxygen, the coolant in an HTR passes continuously over graphite fuel elements at temperatures in excess of 1,000° C, and any impurities present in the helium are rapidly equilibrated with this hot carbon to produce a « reducing » and « carburising » atmosphere comprising predominantly hydrogen and carbon monoxide with traces of water, carbon dioxide and methane. The oxidation potential in a VHTR is expected to be in the range 10^{-20} to 10^{-30} pO_2 equivalent, whilst the carbon potential will be such that chromium and other metals less noble to carbon will be carburised [2]. The very low oxygen potential results in the absence of protective oxide films and with certain alloys containing titanium and aluminium, in selective internal oxidation [3]. Carburisation results from the presence of carbon monoxide, methane and water, and is one of the more important phenomenon associated with the deterioration of metals and alloys used in the primary circuit above about 600-650° C. The presence of methane is particularly important as, in addition to its role in carburisation, it can also lead to a mass transfer of carbon. Methane is formed by a reaction of hydrogen with graphite in the temperature range 400-650° C: this reaction only becomes significant due to the catalytic action of irradiation. The methane formed however, is thermally unstable; it decomposes on surfaces in excess of 800° C, leaving a deposit of carbon. Experience with operating HTR's having a gas outlet temperature in the range 700-750° C has shown that the above processes lead to a concentration of methane approximately 10 % of the total hydrogen present: with higher outlet temperatures it will be lower due to the increased pyrolysis of the methane on the high temperature graphite. Both these phenomena, *i. e.* carburisation and carbon mass transfer are, at the very low levels of methane prevailing in the primary circuit, concentration dependent, and as each must be reduced to a minimum, methane and the hydrogen from which it is formed must be very carefully controlled.

At the hydrogen partial pressures and temperatures prevailing in a steam/methane reformer, contamination of the primary circuit helium by hydrogen diffusion through the tube walls is inevitable, its degree depending on the maintenance of continuous protective films on the « process » side of the reformer tubes and connecting « pigtails » [4]. Now internal oxidation and carburisation are recognised phenomena associated with the failure of reformer tubes. This may well be due to overheating — an event virtually impossible with a nuclear heat source — but since carburisation implies that no protective film is present (carbon cannot penetrate a protective oxide film) it is difficult to see how one could prove that such protective films prevail over the whole life of the plant ! This emphasises the importance of maintaining protective oxide films on the process side of the plant unless alternative economic ways of avoiding carbon mass transfer and carburisation can be found.

An equally serious source of contamination of the primary circuit by process gases arises if it is decided, as one would expect, to maintain a pressure differential between the two circuits such that, should any leaks occur, there is no possibility of fission products escaping into the process gases. It would seem unlikely that such a plant as is being discussed in this paper could be fabricated and maintained without leaks. It follows therefore that consideration of the design, materials and method of fabrication of an intermediate heat exchanger appears to be an essential part of any NPH feasibility study.

Under normal operating conditions it would not seem that « fission product » and tritium activity in the process gases would represent a significant hazard. However, fault conditions will require detailed analysis and this is an area of work which may well influence the design philosophy of the whole plant. It is fully appreciated that such a unit has a far reaching influence on the overall economics of the system, but work to overcome the many problems should be put in hand as its elimination can only be justified by quantitative analysis of the design and operational specifications.

3. BASIC PRINCIPLES INVOLVED IN THE CONCEPT

The primary purpose of having an intermediate circuit is to provide a bridge between the reactor and the chemical plant. This bridge should involve a minimum resistance to heat transfer with a maximum resistance to cross contamination of the HTR helium coolant and the process gases. To achieve this objective it is proposed to use helium as the heat transfer medium to which is added appropriate oxygen containing additives to develop and maintain continuous oxide films. These films would be optimised to have a maximum resistance

to hydrogen diffusion, not only from the reformer tubes but also into the primary circuit. An associated purification plant could be incorporated to control any significant diffusion and leakage from the process side as well as for monitoring and, if necessary, cleaning up fission products coming from the primary circuit.

The composition and concentration of the gases to be added would be dependent on the specific materials used in the circuit and on the operating conditions. The final specification would result from experimental work with the chosen alloys to determine the most effective barriers to hydrogen diffusion. Concentrations are not likely to be more than a few parts per million so that the properties of helium as a heat transfer medium would be unaffected. It is important to appreciate that the normal oxide films formed in air on the stainless and super-stainless steels are not fully protective at temperatures in the 900-1,000º C range, although the high nickel-chromium alloys would be expected to behave well. However, this factor must not be neglected during the development of advanced alloys, and in the choice of prevailing alloys for the « chemical » side of the circuit.

The simplest additive would undoubtedly be pure oxygen, its potential being maintained by its partial pressure. Other oxygen containing gases such as oxides of carbon, oxides of nitrogen, water, etc. might prove more effective. It is quite possible that a different gas or concentration might be more appropriate for the initial formation of the film than that to maintain its integrity.

With only a few parts per million of oxygen containing additives present, any leakage into the primary circuit would not present a significant hazard either to the operation or safety of the reactor, whilst contamination of the process gases can be neglected. Continuous monitoring of this circuit would define the nature and extent of any leakage and would provide that information necessary to make a logical decision when the plant should be shut down for repair.

4. DESIGN REQUIREMENTS

When considering the feasibility and appropriateness of alternative design concepts, a knowledge of certain specific properties, such as the 10^5 hours stress rupture life is essential. As the design develops various problems will arise, some of which can be solved by design changes, others by the use of alternative materials. It is inevitable that some problems, specific to the particular design requirement will remain, and it is to such problems that development work must be directed. However, it is not possible to carry out a large programme of data acquisition, just in case the results might be needed. The major problems are usually design related and therefore the metallurgist and designer must proceed together to ensure that the results are effective. Such design related work is inappropriate to an international organisation, but ultimate success depends on a general knowledge of materials behaviour and it is this general area of basic data related to the various modes of failure where information is so badly needed.

On designing this type of component the following factors must be taken into consideration:

a) *Physical properties:* — Thermal conductivity; — Thermal expansion; — Specific heat.

b) *Mechanical properties:* — Modulus of elasticity up to operating temperatures; — Creep data — including stress-strain-time relationships, stress rupture and rupture ductility at both room temperature and operating temperatures on virgin and « aged » material; — Fatigue data — including low and high cycle fatigue at operating temperatures, the effects of « hold times » and of the environment, particularly after long periods in service; Fretting characteristics under operational conditions including the effect of the environment on virgin and « aged » material; — Notch sensitivity on virgin and « aged » material; — Damping capacity at operating temperatures.

c) *Chemical properties:* — Corrosion, oxidation carburisation, etc. Diffusion data; — Suitability to take coatings for resistance to corrosion, friction and fretting.

d) *Effects of fabrication procedures:* — Influence of cold work; — Influence of welding procedures; — Effects of subsequent heat treatment and service conditions.

A knowledge of the above is necessary to assess the significance of the various failure mechanisms known to be responsible for breakdown of this type of plant. The majority of failures in fossil fired plant are associated with overheating, a phenomenon far less significant in the NPH application: corrosion is also a major cause of failure, and account must be taken of the influence of carburisation and internal oxidation on crack formation and propagation originating at the surface. Design related phenomena include failures resulting from vibration, fretting and fatigue whilst material related failures can originate from thermal stress and stress relaxation phenomena.

No experience of large helium/helium heat exchangers exists, and it is therefore necessary to relate the accepted failure mechanisms occurring in conventional plant, to the basic properties of the materials to be used. Furthermore, these properties must be relevant to the specific environment as so many failures are associated with surface phenomena.

It is therefore clear that for a realistic feasibility study, stress rupture data, even if obtained in the correct environment, is at best an approximate and unreliable guide on which to base a design decision, and that properties such as thermal fatigue, relaxation, fretting and high cycle fatigue are of equal or even greater significance to operational behaviour.

5. METALLURGICAL REQUIREMENTS

It is a basic law of science that at temperatures in excess of about 0.5 T_m (where T_m is the melting point in ºK) the atoms in the metal lattice become mobile, and structures dependent on non equilibrium conditions

cannot be maintained indefinitely. At temperatures in excess of 750-850° C the major problems, associated with the use of the conventional stainless steels and nickel alloys, are undoubtedly associated with metallurgical stability. This is dependent not only on thermodynamic considerations but also on kinetics, particularly on diffusion rates of solute elements — whether present as alloying elements (in the specification) or as a result of the manufacturing process. HTR helium can be both oxidising and carburising to certain elements, furthermore surface reactions lead to both surface and internal oxidation as well as to carburisation, and it is the diffusion of these elements (*i. e.* carbon and oxygen and possibly nitrogen) into the « body » of the metal with consequent structural changes that can either improve or impair the resistance to deformation and fracture: the effect of dechromisation and other elements at the surface must also be taken into account. With most conventional applications, such as with the steam cycle for electricity generation, it is possible, by employing the appropriate design philosophy, to keep metal temperatures down to a value where the structural changes are minimal or are at least confined to the surface so that the « body » of the metal is unaffected by the environment. With the temperatures presently envisaged for the NPH application, *i. e.* up to 950-1,000° C, diffusion from the surface into the conventional high temperature alloys is so rapid that significant structural changes up to 10 mm from the surface must be expected within the design life of the plant. It is therefore essential to use only those alloys whose structural stability — and therefore mechanical stability — is not significantly impaired by carburisation and internal oxidation. It is this problem that must be solved by the metallurgist if he is to ensure a future role for the VHTR.

Electricity generation demands high stresses in certain primary circuit materials, *e. g.* turbine blades and superheater tubes. The process heat application, on the other hand does not involve such high stresses; but the temperature is some 200-250° C higher. One is therefore faced with an entirely different requirement, and it is therefore not surprising that few, if any, alloys are available that, in the authors opinion, are adequate for the NPH application. This, however, does not mean that they cannot be developed within a reasonable time scale. There has been no demand for alloys specifically tailored to this unique requirement, and it would be surprising if appropriate alloys were available. After all, new alloys such as « Zircaloy » and « Magnox » were necessary for the introduction of nuclear power, in the same way as high strength aluminium and nickel alloys had to be developed for the aviation industry.

Some of the basic principles of alloying, with particular attention directed to the behaviour of the individual elements in the stainless steels and nickel alloys have already been discussed in a recent paper by one of the authors [5] and no useful purpose would be served by repetition. One factor is however noteworthy: it concerns activity. Almost all the high strength nickel base solid solution alloys contain either cobalt or tantalum (*): these are activated by irradiation to produce a γ-emitting product. Although they are outside the core the possibility of oxide scale becoming entrained in the coolant gas, being activated on its passage through the core and then deposited in corners and crevices in the primary circuit outside the core cannot be ruled out. The consequence of such activity outside the shielded area would be so embarrassing that it must be avoided; it may therefore be necessary to specify a maximum cobalt and tantalum content for all primary circuit materials thus eliminating these elements as acceptable alloying additions. Alloy development is already in progress but if it is accepted that higher strength alloys having structures stable over their expected operating life in environments envisaged are necessary, then development on the appropriate scale must be put in hand as a matter or urgency, with attention being directed to the use of alloying elements such as tungsten and molybdenum as major alloy additions.

6. *DISCUSSION AND CONCLUSIONS*

A high integrity 3,000 MW (th) gas/gas heat exchanger operating as part of the primary circuit of a nuclear plant is an entirely new requirement, and much time and effort will be required to prove its feasibility. The fact that a nuclear heat source is involved directs attention to safety and reliability. Furthermore, the explosive nature of the product gases — hydrogen and carbon monoxide — with air, — provides a further hazard that cannot be neglected.

It is generally accepted that safety of nuclear plant can only be demonstrated by detailed analysis involving a knowledge of behaviour under both normal and fault conditions. For this much basic data and knowledge of failure mechanisms is necessary; furthermore safety analysis and licensing involve the use of design codes. It is therefore necessary, when modifying an existing alloy (*e. g.* the substitution of Co or Ta by other elements) or developing a new alloy, to work in conjunction with the appropriate safety and licensing authorities from the beginning to ensure that the relevant data is obtained before it is needed. Where 100,000 hours data is required this is not an easy task: attention must be directed to reliable methods of prediction and this in turn requires data on the quantification of failure modes.

The very high capital cost of a nuclear heat source focuses attention on reliability as « outage time » costs far more than with a fossil fuelled plant, and as reliability will inevitably decrease as the upper limit of temperature is approached some conservatism in the design is prudent.

Finally, let us consider an intermediate heat exchanger in the size range 500-3,000 MW (th) fabricated in

(*) Apart from alloys containing Ta as a specific alloying element, it is also present in niobium containing alloys: *Commercial* Nb contains 1-2 % Ta.

Incoloy 800 type alloy. Very considerable experience of design, construction and operation of superheaters using this material exists and one can therefore make a reasoned estimate of its maximum operating temperature. The stress resulting from the very small pressure difference is so low that it can be neglected; it is vibrational and thermal stresses that are limiting. It is estimated from the data available for « Alloy 800 » that the maximum inlet temperature from the reactor is in the range 750-775º C and assuming a 50º C temperature drop across the exchanger, the maximum temperature to the process would be 700-725º C. On the basis of 100,000 hours stress-rupture data alone, and neglecting the importance of all other characteristics, it follows that, with the strongest solid solution type nickel alloy (at these temperatures) available today, *i. e.* Inconel 617, which incidentally contains 12.5 % Co, these temperatures become:

a) From the reactor 850-875º C.
b) Into the process 800-825º C.

Inconel 625 and Incoloy 807 would have a temperature advantage over « Alloy 800 » of about 50º C.

Further work to confirm the above estimates is of course necessary as part of any feasibility design study, the overall objective being to provide the basis of the experimental development programme. This initial design study should take into account the relationship of design philosophy to material property requirements as well as the significance of the specific environments on those properties of importance to each specific component in the plant. Design limitations must be based on the appropriate failure modes taking into account long term operational exposure (30 year life) in the environment, the operating temperature and temperature transients, as well as those effects due to the high velocity helium (*i. e.* the acoustic noise problem) which are absent in a conventional fossil fuel fired heat exchanger.

Following the completion of this feasibility design study it should be possible to specify the precise material properties necessary to achieve the efficiency demanded by the chemical possesses, and to relate these properties to those of prevailing alloys. If prevailing alloys are inadequate the development objectives can then be clearly defined or assessed.

If the estimates given in this paper are realistic it would suggest that a major effort to eliminate the intermediate heat exchanger is desirable and that it would be more rewarding to direct effort to materials and design of the process plant and to the process itself in order to provide the reliability and safety required of a direct cycle nuclear process heat plant.

* * *

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ACKNOWLEDGMENTS. — The authors would like to acknowledge the very considerable help given by their friends and colleagues during many hours of discussion: without this help the paper could not have been written.

Rev. int. Htes Temp. et Réfract., 1976, t. 13, pp. 217-223

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MATERIALS FOR STEAM GASIFICATION OF COAL WITH HTR HEAT

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1. *INTRODUCTION*

This paper on the selection and development of suited metallic heat exchanger materials for coal gasification describes the work which is done in cooperation at Mannesmann and Bergbau-Forschung. The first sections give a survey over the new gasification technique and show the concept and technical realization of steam gasification with nuclear heat and, resulting from this, the main problems for research and development. The last section describes the status of the materials testing and development programms.

2. CONCEPT AND TECHNICAL REALIZATION OF STEAM GASIFICATION

Steam gasification is highly endothermic. In all conventional plants coal serves as raw material for gas and as a source of reaction heat, the heat for steam raising, and other energies needed at the plant. By using the process heat from gas-cooled high temperature nuclear reactors it is possible to avoid using coal as a supplier of heat and instead use it as a raw material for producing gas. The advantages are lower costs of gas production compared with conventional processes in countries with high price rates for coal, the saving of coal reserves and production of smaller amounts of carbon dioxide in the gasification plant.

The main problems to be solved to make possible the large-scale application of nuclear energy to coal gasification can be summarized in the following three points:

— development of high temperature nuclear reactors with helium outlet temperatures of at least 950° C ;

— transfer of the heat from the core of the nuclear reactor to the gas generator;

— design of a suitable allothermic gas generator in which the gasification kinetics and heat transfer and also the materials available for the heat exchanger must be taken into account.

The work of the Bergbau-Forschung concentrates on the solution of the last two points and in the present paper the state of the experiments and other investigations carried out to this end will be presented.

The concept and design of a nuclear plant for coal gasification depends mainly on the way in which the high temperature heat can be introduced into the gas generator at a large-scale. At the start of the development work various methods were analyzed and partly experimentally studied. According to the present state of knowledge the process scheme shown in figure 1 appears realizable [1, 2]: the heat produced in the nuclear reactor and removed at 950° C by a helium circuit is first transfered to an intermediate circuit. This passes through a heat exchanger which projects into a fluidized bed of coal and steam in the gas generator and transfers its heat through the heat exchanger surfaces. The residual heat is utilized for steam generation. Part of this steam serves as process steam for the

gasification and in various stages of gas preparation and conversion plants.

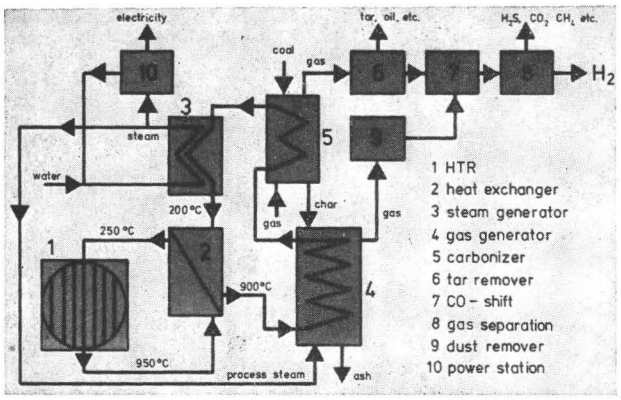


FIG. 1. — *Hydrogen production by steam gasification of coal using nuclear heat.*

Another part is utilized for electric power generation. The helium circuit of the nuclear reactor as well as the intermediate circuit and the gas generator are operated at a pressure of 40 bar. The raw gas produced in the gas generator is converted into synthetic natural gas or other products.

The intermediate circuit separates the nuclear part of the plant from the gasification unit. Thus, it involves a higher degree of security of the total plant, an inhibition of the permeation of hydrogon from the gasifier into the core of the reactor and of tritium from the nuclear part into the gas generator. Moreover, the possibility of an easier replacement of parts of the gasifier is given. But its disadvantages should not be overlooked, *i. e.* a loss in temperature of say 50° C, additional problems in building large He-He heat exchangers, and the enormous costs. On the whole, it is felt that an intermediate circuit is necessary to make the combination of an HTR and a gasification plant feasible.

3. BASIC CONCEPTS AND FEASIBILITY OF THE GASIFIER

A large-scale gas generator in which about 50 t/hour of coal are to be gasified requires an heat exchange surface of about 4,000 m². A proposal for this apparatus based on the experimental work of the Bergbau-Forschung over the past few years is shown in figure 2 [3]. It consists of a horizontal cylindrical pressure vessel of about 30 m length and 7 m diameter. In its interior is a trough, its walls representing the inlet tray for the steam entering the fluidized bed from below. The heat exchanger tubes through which the helium of the intermediate circuit flows project from above into the fluidized bed bounded by the trough. According to present ideas the coal — possibly after preliminary low temperature carbonization — is introduced at one end of the gas generator. It moves in the longitudinal direction through the fluidized bed and is increasingly gasified. The ash accumulates at the other end and can be

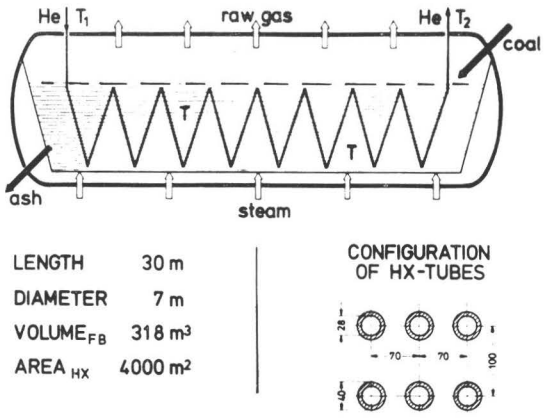


FIG. 2. — *Main features of an industrial gasifier.*

removed through an opening at the left hand end of the fluidized bed trough. The feasibility of this proposal has been checked and confirmed in cooperation with Mannesmannröhren-Werke AG, Düsseldorf.

4. PROCESS CONDITIONS IN THE FLUIDIZED BED

The working conditions of the heat exchanger in the fluidized bed are shown in more detail in figure 3. On the left hand side the heat carrier gas of the intermediate circuit is shown at temperatures of 900 to 1,050° C corresponding to various outlet temperatures of the HTR from 950 to 1,100° C. The results today confirm the assumption, that about 50° C are needed for the heat exchange in the intermediate heat exchanger and again 50° C from the intermediate loop into the fluidized bed.

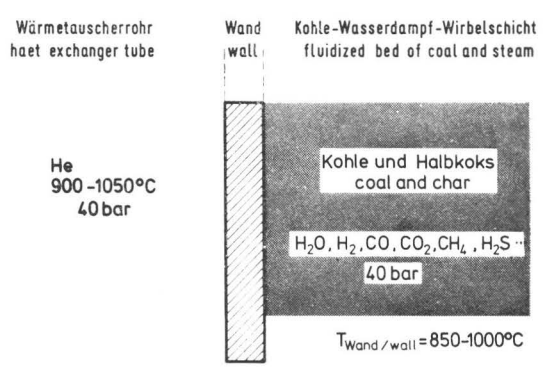


FIG. 3. — *Conditions for the heat exchanger material.*

On the right hand side in figure 3 the conditions of the process side are shown. The fluidized bed operates at 40 bar and at a gasification temperature of about 800° C. The temperature of the heat exchanger surface, therefore, will be between 850 and 1,000° C. This temperature is critical, as the alloy is attacked from this surface.

The various attacking processes originating from the fluidized bed of coal and steam are firstly governed by

the coal. It consists of organic material, minerals (ash), and absorbed water. The ultimate analysis is listed in figure 4.

Composition of German run-of-mine coal:

	hard coal	lignite
organic matter	30-80	37
moisture	3- 5	60
ash	20-70	3

Ultimate analysis of the organic matter:

C	83 - 93	68
H	3,5-5,5	5
O	2- 8	25
S	0,4-0,9	0,5
N	1,4- 2	1

FIG. 4. — *Composition of coal and lignite (weight %).*

When coal is heated up to the gasification temperature pyrolysis occurs and it is converted to char. Carbon and hydrogen are the main components. The char has less hydrogen due to loss by pyrolysis. By contrast lignite contains less carbon and a considerable amount of oxygen (25 %). It should be pointed out, that fortunately the content of sulphur in the German coal is relatively low compared for instance with US coal, which contains in general about 5 % of sulphur.

Normally the ash content of a hard coal for gasification would be about 10 %. The composition varies over a wide range as shown by figure 5. The main components of the hard coal ashes are SiO_2, Al_2O_3, Fe_2O_3, the rest is contained in low concentrations below 10 %. A survey of trace elements of possible importance shows, that the content of chlorine is about 0.08 % and of vanadium 0.005 %. Brown coal ash contains considerable amounts of CaO and MgO.

	Char made from		
	hard coal Hagen	hard coal Leopold	Rhein. brown coal
SiO_2	36,4	41,4	8,2
Al_2O_3	22,0	25,9	4,6
Fe_2O_3	28,5	16,9	9,5
TiO_2	1,0	0,9	0,4
CaO	3,5	3,7	34,6
MgO	0,9	1,2	13,2
Na_2O	2,1	1,1	0,8
K_2O	2,3	3,2	0,4
P_2O_5	0,1	0,2	0,1
SO_3	2,4	3,6	5,6
Σ	99,2	98,1	77,4

FIG. 5. — *Ash analysis (weight %).*

The gaseous phase in the fluidized bed is produced mainly by the reaction of the steam with the carbonaceous solids, in which part of the steam is used for [redacted] duction of H_2, CO_2, CO, CH_4, etc. A typical [redacted] position at 40 bar and 750° C is:

Steam content: 50-70 %.
Dry gas: H_2 CO CO_2 CH_4 H_2S
60 19 18 2 0.3 Vol. %.

The primary component in each case is the steam which generally can be converted to a degree of maximum 50 %.

5. FURTHER DEVELOPMENT OF THE GASIFIER

The gasification power of an allothermal gas generator can be determined from the heat balance because such a temperature is produced in the gasifier and the heat consumed by the gasification reaction is equal to that transfered from the medium of the intermediate circuit into the fluidizing bed, *i. e.*

consumed heat = transferred heat.

To solve this equation it is necessary to have the gasification kinetics data, which essentially influence the left-hand side of the equation, and heat transfer data.

Work on this field is done at Bergbau-Forschung since 1969 in several experimental devices which are shown schematically in figure 6. In this picture is demonstrated the stepwise development of the gas generator for steam gasification from laboratory scale to prototype size.

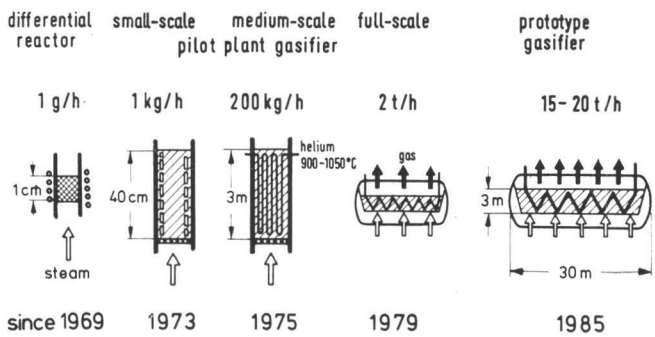
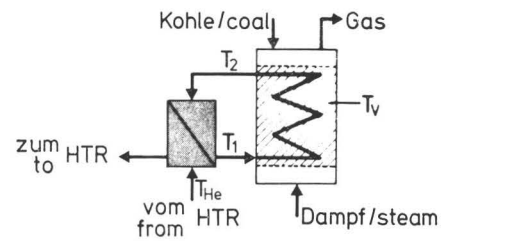


FIG. 6. — *Full-scale commercial gasifier: steps of development.*

Basic data for the reaction rate and the heat transfer have been measured in the first two devices shown in figure 6. Since 1969 the reaction kinetics of gasification with steam and hydrogen of different coals and chars have been investigated in a small fixed bed at temperatures up to 1,000° C, and total pressures up to 70 bar. Since 1973 Bergbau-Forschung has operated a small-scale pilot plant having already an internally heated fluidized bed at 40 bar. This unit has given the first results concerning reaction kinetics, gas composition and heat transfer under realistic conditions. The transferability of the results and conclusion has to be confirmed in the bigger units, where the interplay of kinetics and heat transfer can be measured on an increasingly realistic scale.

With the kinetic, heat transfer and specific heat requi[redacted]nt data measured until today in the differential

reactor and in the small scale gasifier, the throughput of the commercial gasifier shown in figure 2 can be calculated by solution of the heat balance equation mentioned above. Relevant data is listed in figure 7 for helium outlet temperatures in the range from 900 to 1,100º C which demonstrates the enormous effect of rising He-outlet temperature on coal throughput of one gasifier [4].



T_{He}	900	950	1000	1100	ºC
T_1	850	900	950	1050	ºC
T_2	809	821	833	850	ºC
T_v	759	771	783	800	ºC
Kohledurchsatz coal throughput	39	47	55	70	t/h

FIG. 7. — *Data of a gas generator.*

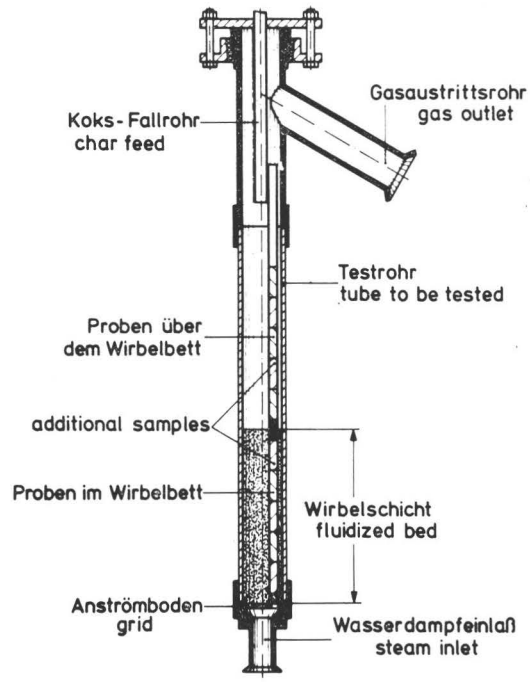


FIG. 8. — *Set up for corrosion test.*

6. MATERIALS DEVELOPMENT

One of the priority tasks is the development of a suitable alloy for the heat exchanger, which withstands corrosion, shows sufficient creep rupture strength and allows tube forming. Under these aspects experiments are underway, in which corrosion test devices for material testing under realistic conditions in a fluidized bed of char and steam are operated. The primary step in these investigations is to find a material with sufficient corrosion resistance [5, 6].

The conditions, under which heat exchanger materials are operating were discussed by means of figure 3 in section 4.

The wall temperature at the surface, being in contact with the fluidized bed, will be between 850 and 1,000º C. This temperature is decisive for the attack from this surface.

To simulate the conditions in the fluidized bed, a laboratory scale gasifier was built. Samples of alloys available on the market have been tested in a small fluidized bed under atmospheric pressure, in which 50 to 100 g/hour of char is gasified by steam. The setup of the testing device and the location of the samples are shown in figure 8. The main piece to be examined is a tube of 48 mm in diameter and 3.5 mm wall thickness. At the bottom of the tube a plate with holes is located, through which steam can be introduced. By this a fluidized bed is operating in the interior, so that the inner wall surface acts as a testing area for the corrosion attack from the bed and from the gaseous phase above the bed as well. Besides several smaller pieces (8.3 mm diameter and 15 mm length) of alloys to be tested can be introduced into the bed.

The total apparatus is shown schematically in figure 9. The small testing gasifier is heated electrically by

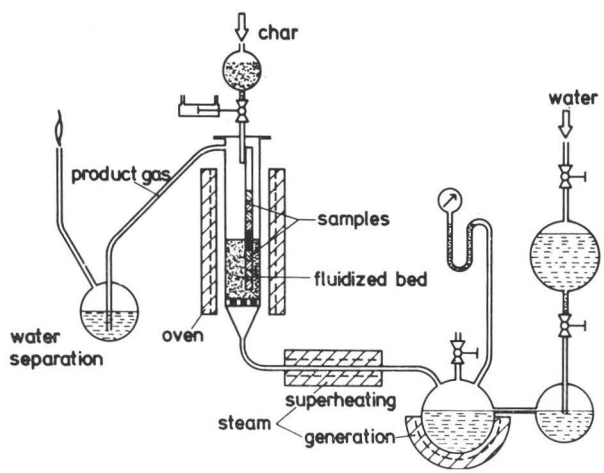


FIG. 9. — *Device for corrosion tests.*

oven, the temperature of the fluidized bed itself being between 950 and 1,000º C and above the bed some 1,050º C. The apparatus is fully self-acting, so that it normally is in day and night operation, in order to get the necessary high number of testing hours in a reasonable time.

In the fluidized bed the following known steels and alloys were first tested: ferritic Cr-Al-Si-steels, austenitic Cr-Ni-steels and Cr-Ni-alloys. Ferritic-Cr-steels could not be used, because of their creep rupture values at higher temperature and because their impact at room temperature is very low. Nevertheless some corrosion tests with ferritic-steels were made, with the negative results expected.

Beside the above a systematic development of new alloys was initiated. Since steam is the main component [illegible] the fluidized bed in the steam gasification process, [illegible]lective corrosion tests with all new alloys were [illegible] steam at 1,050º C.

Chromium is the main element to prevent oxidation of materials at high temperature. Under the attack of atmospheres with a high content of oxygen or oxidative components chromium builds up a protective oxidic scale at the surface of chromium containing alloys.

Other alloying elements, which will influence the properties of this protective film are Al, Si, rare earth metals, Ni a. s. o.

To increase the creep rupture strength, the materials were alloyed with C, Mo, W, Co, Ti and Nb. All these elements will also influence the oxidation properties of the alloy.

The aim of these investigations is to develop an alloy with a sufficient oxidation-resistant behaviour. One assumption for this is the building up of a protective oxidic scale with a small oxidation rate and nearly uniform oxidation.

At the high test temperatures in all cases of known high temperature alloys more or less nonuniform oxidation has been noticed. In some cases there was found a preferential oxidation of the grain boundaries, in other cases internal oxidation took place.

An example for uniform oxidation combined with a small attack along the grain boundaries and internal oxidation is given in figure 10. This steel was exposed to the fluidized bed for 1,000 hours at 1,050° C.

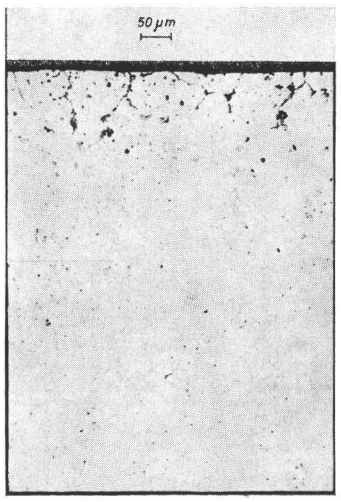


FIG. 10. — *15 CrNiSi 25 20, gas room 1,050° C, 1,000 hours.*

The influence of oxidation extends to a depth of 0.3 mm. This type of internal oxidation is representative of silicon alloyed heat resisting steels.

Nearly the same oxidation characteristic was to be seen in alloys with additions of Titanium or Zirconium.

Aluminium (fig. 11) increases the depth and intensity of internal oxidation in a characteristic manner. The internal oxidation is penetrating into the material preferably in vertical paths from the surface. We have found a similar oxidation in all alloys with aluminium contents of 1 to 3 %. In this case we have 1.85 % of Aluminium in the alloy.

In steam tests up to 5,000 hours the penetration of internal oxidation into Al containing alloys was analysed (fig. 12). Small additions of Al or Zr increase the penetration speed to a great extent as can be seen from figure 13, where the values of 3 chromium-nickel-alloys are compared. It must be mentioned in this case that the intensity of internal oxidation in the Al containing alloy is very much heavier than in the Zr containing alloy.

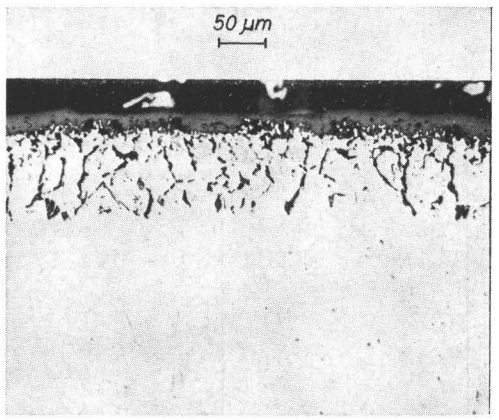


FIG. 11. — *X 5 NiCrAlTi 34 20, fluidized bed 980° C, 1,000 hours.*

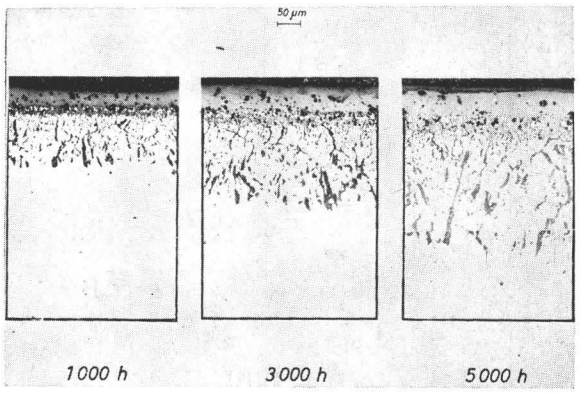


FIG. 12. — *Internal Oxidation in H_2O at 1,050° C, 25 Cr 30 Ni 2 Al.*

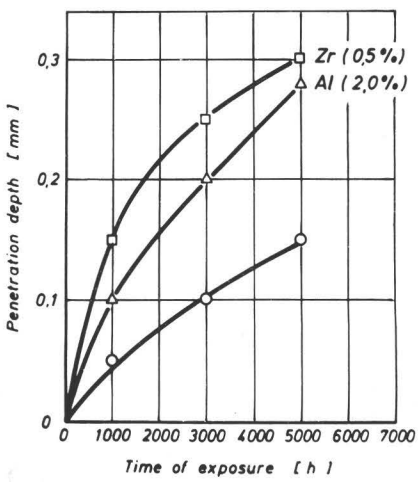


FIG. 13. — *Internal oxidation in H_2O at 1,050° C.*

Heat resisting cast steels include high C-contents to increase the creep rupture. By this high carbon content the heat resistance of the grain boundary will be lowered as can be seen in figure 14. The attack of the grain boundaries extends up to 0.9 mm from the surface under the same oxidation conditions of 1,050º C in the gas room, of the fluidized bed equipment.

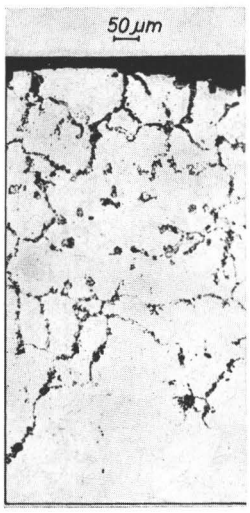


FIG. 14. — *G-X 40 CrNi 25 22, gas room 1,050º C, 1,000 hours.*

Alloying with Nb of the same cast steel type leads to higher creep resistance by building up a Nb (C, N)-eutectic network. But oxidation proceeds preferably also at the paths of Nb (C, N), figure 15.

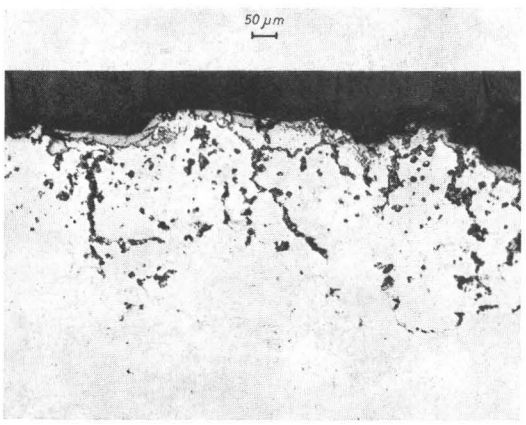


FIG. 15. — *G-X 40 CrNiNb 25 24, gas room 1,050º C, 1,000 hours.*

We have found similar oxidation characteristics in all the other alloys with additions of cobalt, molybdenum, tungsten, aluminium and titanium. One speciality in the behaviour is shown in figure 16. In this very complex alloy no carbides will be found in a surface zone of 0.15 mm thickness. It can be assumed that the concentration of carbide building elements is lowered by their diffusion to the surface, where these elements are consumed through the building up of the oxidic scale.

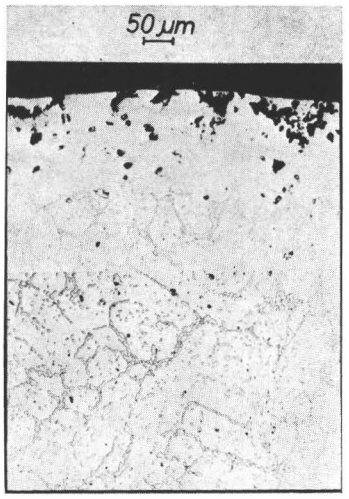


FIG. 16. — *G-X 50 NiCrW 36 26, gas room 1,050º C, 1,000 hours.*

Furthermore decarburisation in this zone occurs in all alloys with higher carbon contents (fig. 17). The amount of decarburisation depends on the temperature, the time of exposure and the partial pressure of the oxidizing gas.

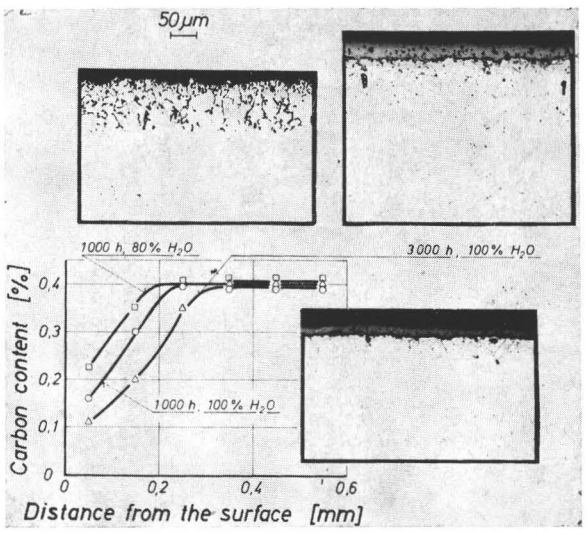


FIG. 17. — *Decarburisation at 1,050º C, X 40 CrNi 25 20.*

One could think that a further increase of the chromium content would be profitable for the development of heat resisting steels. But as it can be seen by the oxidation behaviour of the known 50 Cr-50 Ni cast alloy (fig. 18), no benefit resulted. Even in this alloy small amounts of Zirconium have intensified and changed the appearance of internal oxidation in a characteristic manner, which is independent from the base of the alloy. Also the substitution of nickel by cobalt shows no advantages.

The composition of the oxidic scale and the oxidic internal particles will give us some information about the oxidation mechanism.

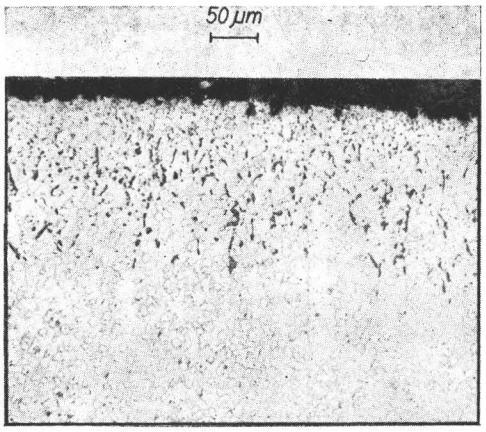


FIG. 18. — *X 5 CrNi 50 50, fluidized bed 980° C, 1,000 hours.*

In figure 19 and 20 the spot analysis will give an impression of what happened during oxidation within a period of 3,000 hours at 980° C. Higher concentrations

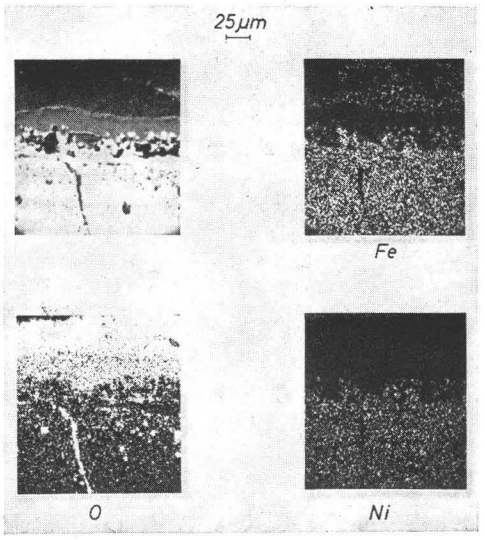


FIG. 19. — *X 10 NiCrAlTi 32 20, fluidized bed 980° C, 3,000 hours, spot analysis.*

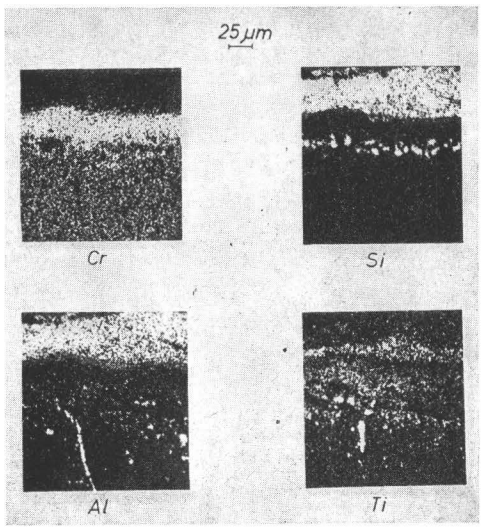


FIG. 20. — *X 10 NiCrAlTi 32 20, fluidized bed 980° C 3,000 hours, spot analysis.*

of oxygen can be seen in the surface area and in the grain boundary. In the scale an enrichment of Cr and Al can be noticed. The Si-rich layer on the oxidic scale is a deposit of ash. The internal oxidic particles have a higher content of Si, Al and Ti. Cr does not participate in the formation of these particles.

CONCLUSION

Concluding it can be said:

Under the specific conditions in a fluidized bed of steam gasification equipment, known heat resisting alloys have shown different oxidation mechanisms.

Silicon and carbon favour the oxidation of grain boundaries. In alloys with Co, W, Mo, Al and Ti internal oxidation partly combined with oxidation of the grain boundaries takes place. During the testing period of 1,000 hours there is no indication of carburization, sulphidation and attack by hydrogen or ash in all tested alloys.

As to erosion, the experiments have shown that its effect on the material seems to be negligible, as we have small, light particles and very low velocities (0.1-0.2 m/s) in the fluidized bed. The importance of H and T permeation is also reduced, whenever oxidic scales inhibiting this process are built up. After these results it should be possible to develop alloys which will have sufficient heat resisting and creep rupture strength to secure the required lifetime of the heat exchanger. The next steps in our development will be to increase the oxidation resistance and the creep rupture strength by such alloying elements which will allow a good processing, especially the tube making of the material. On the other hand the price of this material should be low enough for the process to be economic.

* * *

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DISCUSSION

SECTION 2

S. F. Pugh. — The behaviour of a material, particularly in a slightly novel condition of exposure, can be effectively dominated by trace elements. Because of the way materials get recycled, certain unexpected impurities build up. One has to do empirical work to reveal how important this is. Almost invariably the specifications do not mean very much when it comes to defining behaviour of materials. It is normally necessary to work within a specialized composition range within the overall specification. High temperature gas cooled reactors present novel requirements for high temperature materials. For example manganese is rather a nasty element for circuit contamination and in some cases it has a dominating effect on radioactivity of the circuit. In helium atmospheres exposed to hot graphite there is more worry about carburization probably than oxidation, and so the whole attitude to surface films and contamination of the material in depth is rather special and different.

P. Esslinger. — Dr. Graham, I have noticed with interest that you look at blade materials which we use now in the aircraft industry. But I think here one should put some question marks because of two points. The first one is that these materials are mostly developed for lifes of about 3,000 hours, and I think nobody knows very much about their behaviour for longer times as you are looking for, say 100,000 hours. And therefore you may meet stability problems. The second point is: These alloys (you mentioned for example IN 100 and René 100) have normally, if applied for small components, a high scrap rate. We have a turbine blade which our supplier produced with a scrap rate of about 70 %.

Now this is a very complicated blade, but on the other hand, if you come to blades of other sizes, you may meet porosity problems and so on and you may have much smaller creep strength than you would expect. The second question: You mentioned the high melting point materials, and clearly that is a possible solution for the helium turbine, because there you have no oxidation problems. You mentioned TZM which is a molybdenum alloy, and I wonder why you did not mention niobium.

For with molybdenum you have the problem of brittleness at room temperature, which you do not have with niobium.

L. W. Graham. — I agree with the last point concerning molybdenum but I believe Mr. Huddle will say someting about the poor behaviour of niobium in this atmosphere. In fact, if I had my choice I would go away from the metals for the future in this reactor system. I think the best material for the circuit of this reactor is carbon, especially the use of fibre-reinforced carbons, but I seem to be a mall voice in the wilderness at the moment.

On the point about why we are looking at materials that are used in aircraft: Such materials probably represent the most advanced high temperature applications and are therefore of interest in relation to HTR gas turbines. We also realize that in our business we have to have a certain rapport with the industry, there has to be some basis on which to start. You cannot talk to people on the turbo-machinery side unless it is on the basis of designing something they know about. These materials are very new in themselves and although we recognise the problems of long-term stability, we also have a very special non-oxidising environment which we feel can be used to great advantage to specially develop alloys from the basis of those existing. This is also why we pay great attention to working closely with alloy manufacturers and developers who, in the end, have to produce the materials.

Incidentally, the blade size in a HP helium turbine in an HTR would be much smaller than in open cycle power gas turbines, only of the order of 100 mm.

R. A. U. Huddle. — Can I just add a few words to what Dr. Graham has said ? About 6 years ago we tried niobium alloys in collaboration with ICI. These alloys were completely hopeless because they merely acted as an oxygen getter, they embrittled to such an extent that we could break them by hand ! I would just like to add one very sad thing, and it is sad because I honestly believe that the helium gas turbine is the way to use the HTR. It is of the two alloys that one would like to

choose, that is IN 738 and IN 100, IN 100 has 15 % cobalt and IN 738 has 8.5 % cobalt, and also 1.75 % tantalum which is significantly worse. So it means that even with these alloys we have got to do some development.

P. KOFSTAD. — I would like to comment on a couple of points made by Dr. Graham in his presentation on the behaviour of materials in HTR helium.

One point is the marked difference in behaviour of titanium- and niobium-stabilized steels. In these environments titanium seems to be an undesirable alloy component in that it leads to extensive oxidation, while niobium as an alloy component seems to be unaffected and is not oxidized. This difference is surprising as both metals are strong oxide and carbide formers and in these environments there should be no essential difference between these alloy components. One possible explanation is that a major part of the titanium is present as gamma prime, and as such the titanium component may be both oxidized and carburized in these environments. This has also been demonstrated in various exposures in HTR atmospheres. If most of the niobium is present as niobium carbide, NbC, in the alloy and not in the form of solid solution, the niobium component should be unaffected in these environments, as thermodynamic calculations show that niobium carbide will not be oxidized in HTR environments.

Carburization may prove to be an important aspect of materials compatibility in HTR helium, and I would like to second the plea of Dr. Graham to extend studies of carbon solubility and diffusivity in high temperature alloys. We also need considerably more knowledge on the carbides that are formed; we usually assume the formation of carbides such as TiC, NbC, etc., but should consider the possibility of formation of mixed or complex carbides. As a final point I would like to comment on the effects of aluminium. High aluminium alloys may potentially form protective aluminium oxide films, and aluminium may as such be a beneficial alloy component. On the other hand, aluminium oxide scales are particularly prone to cracking and spallation particularly during temperature cycling. And temperature cycling is involved in all our studies and will be so in operation of HTR reactors; therefore aluminium is not likely to be a beneficial alloy component as far as high temperature corrosion in HTR is concerned. Furthermore, if aluminium does not form a continuous oxide scale, it will promote internal oxidation of the alloys.

R. A. U. HUDDLE. — About 5 years ago after we had the first results of niobium alloys I calculated that the concentration of niobium that one would expect to have in solid solution with excess carbon present (that is, the amount of niobium in solid solution in equilibrium with niobium carbide) and bearing in mind the 10^{-16} partial pressure oxygen I used in the calculation, one concluded that niobium would not oxidize in HTR helium: The same was true for the carbide. Although the calculations were approximate, I do not think they were far out.

P. KOFSTAD. — You really do not have to do that [illegible] culation, because if niobium carbide does not ox[illegible] and if it is in equilibrium with the alloy, the amount of niobium you have in solid solution is not going to oxidize.

A. M. ANTHONY. — I want to make a remark about the use of thermodynamics standard and free enthalpy to understand the oxidation of an element. I think it is not useful in relation to such an alloy, because you do not know really the activity of the element in the alloy. The range of oxygen pressure for oxidation can change by many orders of magnitude; and also you do not get exactly the full oxide in the surface.

R. A. U. HUDDLE. — I do not really agree with that, because I believe that concentration and activity, when you are in the parts-per-million range, are the same. I agree with you that thermodynamics is a very doubtful thing in corrosion: It is kinetics that are important. However it is something one can calculate, and I think if it says it won't go, it does not go unless you have done the wrong calculations.

P. KOFSTAD. — A comment on the use of thermodynamics in alloy oxidation and carburization. One must of course be cautious in the use of thermodynamics in predicting the reaction behaviour of metals and alloys, but there is no reason to be unduly pessimistic in applying this extremely powerful tool. All order of magnitude calculations that we have made as to the formation of reaction products in HTR helium have been borne out by the experiments. But the thermodynamics have to be applied with due regard to kinetics and mechanism of reactions. For instance, carburization of alloys may take place even though the carbon potential of the ambient gas does not predict carbide formation. This is, however, explained — also in terms of thermodynamics — by considering that there is a large oxygen potential gradient in the oxide scale. If the carburizing gas molecules may penetrate into the regions of low oxygen potential, carbide formation becomes possible. This may, for instance, take place if the oxide contains microcracks and porosity; in this case the gas molecules within the porosity do not readily exchange and are not in equilibrium with the ambient gas, and carburization may ensue.

R. UBANK. — I was interested in the apparent improvement in creep life under helium as opposed to air. We have noticed the same sort of improvement at Rolls Royce when we do our test in vacuum.

I wonder if Dr. Graham has tried a vacuum test.

L. W. GRAHAM. — No.

R. KREFELD. — Dr. Kalwa, you considered as a resistance parameter the creep rupture. Now, you are operating your tubes in a fluidized bed and very likely, to expect vibrations, which means that a fatigue damage at least during a part of service time. If you are looking into the risk of rupture (or better probability of failure during service time) and you want to assess this, I would like to know: Do you consider in this case a combined mechanism like the creep enhanced fatigue process which [illegible] takes place?

P. G. KALWA. — I have heard today some questions in this direction, and I think it should be said here that the control of vibrations should be a matter of construction and not a matter of materials development, for I think there is no way to solve this problem by development of materials. It is a matter of construction and a matter of conditions of the heat exchanging areas. Where you have very low velocities, you will not have vibrations. You have an alloy with a protective layer of an oxydic scale. If you bring vibrations into this material, you will produce cracks in this protective scale, and I see no way to give this scale properties making it resistant against vibrations.

H. NICKEL. — Mr. Huddle, at the end of his paper, was very pessimistic by giving us an outlook of which alloys are available, and this in contradiction with Dr. Kalwa's results. I want to ask both of them: What are now your views for the future?

Mr. Huddle mentioned alloy 800 and the maximum process temperature we get by an intermediate heat exchanger to be about 700° C or 725° C. He gave an increase of 50° C by taking Inconel 625 or 807.

We saw from the paper of Dr. Graham the positive influence of the alloys with cobalt. We are very interested in this matter, and although I know the questions coming from the safety commission and the licensing people, my feeling is that we will have the possibility to stay with cobalt. You mentioned that if you have 0.05 %, you would never have a positive answer from the safety commission. My question is, why do you come to 0.05 % ? Is that a solution question?

R. A. U. HUDDLE. — Having been associated with a certain unpleasant experience concerning the activation of tantalum and with previous activation experiences in the U. K. A. E. A. as well as many discussions with the operator of the Dragon reactor experiment, I have come to the conclusion that no responsible user would take the chance of operating a reactor where he can have cobalt radiation outside the shielding of his plant. The reason why I chose that actual figure of 0.05 % was because that is about the figure that is as low as you can go in nickel alloys, without having a significant cost penalty. I did not want to give a figure that was impossible for manufacturers. However if they can supply nickel alloys with 0.05 % cobalt for the Canadian CANDU type reactors (*i. e.* Inconel 600), we ought to be able to do the same. Concerning cobalt in the oxide film, my own experience suggests that one is lucky, at the temperatures we are talking about, if you do not get oxide spalling.

I have seen many specimens where this unprotective oxide film (Dr. Kalwa has just shown us a lot of pictures of great thick oxide films, together with internal oxidation, which implies unprotective oxide films) had little white spots which, when analyzed, were mainly metallic nickel. Now if you have got cobalt in the alloy, these spots will be nickel plus cobalt, and when the oxide comes off, it will go throught the core and become activated. We have not got data concerning the cobalt content, but I know that I would not be a party to any alloy development for the primary circ[illegible] which contained either cobalt or tantalum as an alloy addition, and if you talk to the operators of gas cooled reactors in the U. K. — they have got the experience — I am sure they will support what I have said.

H. NICKEL. — Then let me ask: Why do you have nothing against nickel ? You will have the same situation, you have not an *n*-gamma reaction, you have an *n-p* reaction, you get cobalt acitivity too.

R. A. U. HUDDLE. — Naturally I am worried about nickel, but it is cobalt and tantalum that provide the real hazard. However, I am more worried about these oxide films. We have seen Dr. Kalwa's picture showing carburization and internal oxidation, and I have seen many pictures of other failures all involving carburization and internal oxidation. Now that to me means that there is no protective oxide film, that there is not the sort of film that will stop hydrogen going through. And therefore if you have carburization and internal oxidation, I can only come to the conclusion that we shall be in the regime of clean metal hydrogen permeation.

I am genuinely worried about hydrogen corrosion, because if a significant quantity of hydrogen is coming in, then it is going to corrode the graphite to form methane, and because it is the « low » temperature graphite, that is going to be corroded, that is the reflector graphite, and that is the permanent part of the core that must live there for 30 years. Furthermore we must look into the possibility of carbon deposition on hot spots of the core and its implications.

Now coming back to the temperatures. If anybody were to ask me to take responsibility for building a heat exchanger and to be able to give the necessary guarantees concerning fabrication and service, I want to convince myself it can be done successfully. Concerning the temperature of an IHX what then is the maximum you can operate satisfactorily with alloy 800? Quite independently before I ever spoke to Dr. Fricker on this, I had my own figure written down. He came out with another figure which happened to be identical.

H. FRICKER. — A few degrees higher.

R. A. U. HUDDLE. — Sorry, agreed, but it was so very near. In our paper we have quoted above this original figure, it is 750° C to 775° C. This we think is a realistic and honest figure.

P. G. KALWA. — May I answer to Mr. Huddle's picture of oxidation. I think that we have a somewhat more complicated picture of oxidation than this simple one. Here we have an oxydic layer, and beneath the oxide layer nothing happens. We must see that we have an equilibrium in oxygen content of this steel to the oxydic layers, no chromium will be oxidized in the material. The chromium will be oxidized at the surface, but for all the other elements the oxygen content [illegible] the steel is high enough to oxidize them beneath [illegible] surface. If you have a protective oxydic scale, you [illegible] also have an internal oxidation of these elements.

W. WANZL. — Prof. Nickel had a question concerning the ash analysis of brown coal. The purpose of my picture was to list the ash analysis of hard coal, because until now we have done all our corrosion test with hard coal, and for comparison I have listed an analysis of brown coal.

H. F. NIESSEN. — I like to make a remark on the hydrogen permeation. If you calculate for example with a three times higher permeation rate than we did, then for bright materials you get 50 ppm into our circuit, because of a relatively large purification system. But let us assume we have more hydrogen in the circuit. In that case we go with 10 % through the purification system, that is cheaper than IHX, and I think the only question is, can we convince the licensing authorities.

W. BETTERIDGE. — Can I revert to the entrapment of cobalt in scale. The question was asked whether it would be possible to work to a lower limit than 0.05 % cobalt. Well, carbonyl nickel will contain some 10s of parts per million. Now if you are prepared to have virgin nickel used in the alloys you use, then I am quite sure you could get an appreciably lower limit than 0.05 % cobalt. Probably less than 0.01 % would not be at all difficult. But now let us turn to tantalum, because here I see a much more serious problem, particularly since niobium-containing alloys are being recommended as those least affected by helium atmospheres. Tantalum and niobium, of course, occur together in ores, and, again trusting to memory, I believe that the purest niobium that you can get still contains something in the order of one or two percent of tantalum.

So if you are going to look for alloys with 4 % of niobium in them you will have 0.04 % tantalum, and there is a problem.

L. W. GRAHAM. — I would like to comment on alternatives to materials containing cobalt and then to say something more general. First of all, the alloy that Mr. Huddle mentioned, IN 617, which contains cobalt: The nearest equivalent we believe might be equally acceptable is IN 586. This is why it is on the list of favoured materials, but it is not as strong as 617. Also Hastelloy S is of interest in being cobalt free version of Hastelloy X. We, of course, would like to see higher strength high temperature materials and again look to the alloy producers to get the strength up with something else, perhaps molybdenum or tungsten.

Could I now make a general comment. Today we seem to have split the day into two interesting parts. In the first part we heard from established industry which seems to be quite satisfied with the status and is not willing to spend more than 5 % of a small amount of money to improve anything, certainly not on the time scale we are talking of here. This afternoon we have been talking about devices which in my opinion will not be commercial realities for 20 to 25 years. We seem to have a gap between the oil-crisis induced panic for technical advances in energy and an industry that is not able to find the finance to invest for 25 years ahead without a return. I am suggesting there is only one way to deal with this. The more advanced systems that we have heard about this afternoon must be approached by a series of stepping-stones, the first of which is a commercial exploitation of the HTR for electricity producing systems of high efficiency. To launch this requires a large investment which has not been forthcoming from the type of government investment put in to launch the PWR through the nuclear submarine. Such investment is needed through collective government and industrial effort because of the scale of the requirement.

The gaps between this and the process heat systems can then be filled by progressive efforts based firmly on the broad basis of the power producing systems.

C. EDELEANU. — I am awfully glad that I have not got your problems. The HTR reactor, as far as I am concerned, is the irrelevancy. Every fossil fuel burning power station has gases of about 1,300º C or so in it and these gases are being cooled to steam temperature. This is idiotic. A conventional power station should have a compressor, we should burn under pressure, then take the top temperature off by reforming, ethylene cracking or anything like that. You should then let down through an expander, and get to the temperatures you need for raising steam by conventional means. You then have efficiencies in the 80 %, 85 % range. There are many other ways of filling this gap coming from the other side.

Now to comment on the reformer paper: We have looked at this and see absolutel y no technical problems in building a reformer for these comparatively light duties, but the problem is that the engine that we need, the reactor, does not exist for reasons which Dr. Graham has pointed out. I think we can approach this from the conventional field, adopt the principle which has already been established by Dragon but by using conventional coal burning or oil burning and so on, and meet in 20 years, when you have a reactor.

L. W. GRAHAM. — What is the working fluid that you are talking about for the power turbine?

C. EDELEANU. — Combustion gas.

L. W. GRAHAM. — So you have got to develop a turbine then.

C. EDELEANU. — I cannot see any problem.

L. W. GRAHAM. — If you want such a machine, it is probably a closed cycle helium turbine, fossil heated. Such things are existing. They have got one operating at Oberhausen.

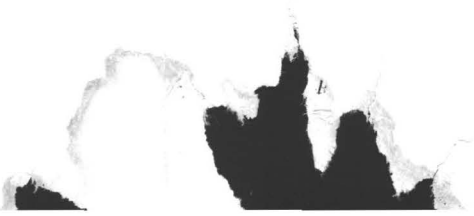
S. F. PUGH. — I think we have come back to the problem that I mentioned earlier. These processes of coal gasification and reforming are achieved with most unreliable gas flames which produce hot spots and deposit many kinds of contaminants at temperatures up to [illegible] C. but on the other hand for nuclear applica-

tions there is grave concern about going much above 700° C with fairly pure helium at a guaranteed maximum temperature. There does seem to be a contradiction. It must arise from very different requirements for reliability of plant. It cannot be in the fundamental properties of materials as such.

H. NICKEL. — We have the same discussion in Germany with our friends from industry. They tell us every time that their systems are working since 15 years. But there is one excellent mistake in it, and that is related to the problem of the combination of the nuclear reactor with these systems. The problem in this case is that the licensing authorities are not interested to see the plant operating for three years, we have to show that you have no accident for the next 30 years, for the life time, and this is our problem on the materials side.

H. FRICKER. — I agree with Prof. Nickel. This is the difference between the two attitudes that have been confronted to each other. I happen to be active on building a steam generator for THTR, and I know approximately what is asked of a constructor of such an equipment, when it is actually built. And I also know what was asked of us a month before we started building it, and these are two entirely different stories. Therefore I can only warn people who want to apply this very valuable heat source, the high-temperature reactor, to things that are too exotic. I think the first step in applying process heat is via an intermediate heat exchanger. I cannot see any licensing authority that would presently permit a direct cycle.

And this is also why we are very careful in stating temperatures. I know I could use alloy 800 at 850° C or may be at 900° C, but I do not think the others would believe it.



SECTION 3

REQUIREMENTS OF ADVANCED AND FUTURE ENERGY CONVERSION SYSTEMS

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 230-236

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HIGH TEMPERATURE MATERIALS REQUIREMENTS OF THE MAGNETOHYDRODYNAMIC ENERGY CONVERSION

By

A.-M. ANTHONY

INTRODUCTION

Electrical power generation by magneto-hydrodynamic (MHD) or magneto-gasdynamic (MGD) converters consists (fig. 1) in driving a conducting fluid at high speed through a perpendicular magnetic field and thereby generating a direct current. This conversion was first made by Faraday using the Thames River as a conductor moving through the magnetic field of the earth. The association of this principle with technical thermal processes has the potential of increasing the efficiency of energy conversion from 45 % to 60 %.

The MHD and MGD processes are classified in three methods depending on the fluids used (table I): the open gas cycle operation uses energy from coal, fuel or natural gas. To make the gas conductive, one adds K and Cs (fig. 2). The temperature is high and the medium rich in oxygen. The closed gas cycle uses an inert gas

Table I. — *MHD processes.*

System	Fluid	T° C	
		Max.	Min.
Open cycle	Coal, fuel, natural gas. . . .	2,400	1,800
Closed cycle	He, Ar heated by nuclear reactor.	1,700	800
	Liquid metals (Na, Hg, NaK). .	900	700

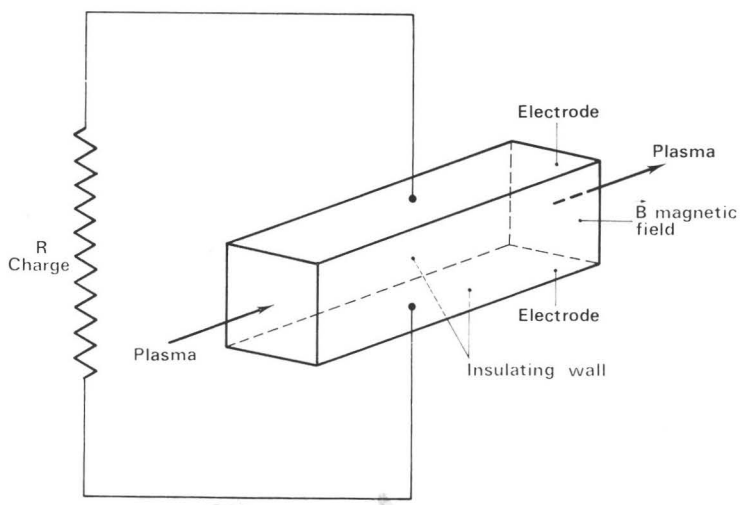

FIG. 1. — *MH[illegible]rocess* [1].

such as He or Ar, heated in a nuclear reactor (fig. 3). The temperature is not as high as before. The liquid metal cycle uses liquid metals instead of gases. As the electrical conductivity of metals is high, this method does not need a high speed of fluid or a high magnetic field. Only the open cycle technique needs high temperature materials. Since 1965, much has been done, and in France a lot of research work has gone on in the materials field. Now the U. S. A., U. S. S. R. and Japan are working with different primary energy sources: liquid fuel in Japan, coal in U. S. A. and natural gas in U. S. S. R. In Europe the research is mostly limited to fundamental aspects.

I. — ELECTRICAL POWER CONVERSION BY THE OPEN CYCLE

The power P generated by MHD is:

$$P \alpha v^2 B^2 \sigma$$

where σ is the specific conductivity of the fluid,
v is its speed,
and B is the magnetic field.

σ is high for fluids at high temperature but in general is not sufficient for MHD. It is necessary to add K and Cs with a small ionization potential. As Cs costs are high, one prefers to use potassium as KOH, K_2SO_4 or K_2CO_3.

To increase B, the solution lies in the use of superconducting materials. In a gas with 1 mole % of potassium salts, the gas speed reaches 1,000 or 1,500 ms^{-1}. The problem of materials at high temperatures concerns the structure of the combustion chamber of the MHD channel and heat exchanger, but the main problem is the life time of electrodes.

II. — PROPERTIES OF HIGH TEMPERATURE MATERIALS

The gas temperature is about 2,500° C; if the wall is in metal, the temperature is 500° C: this is a cold channel operation system. If the wall reaches 1,800° C, it is a semi hot operation system that will be discussed in the following.

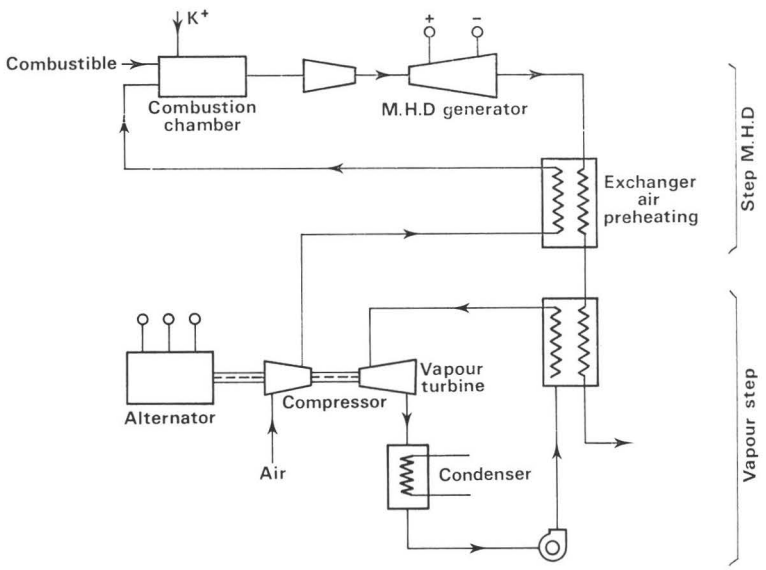

FIG. 2. — *Open cycle MHD process* [2].

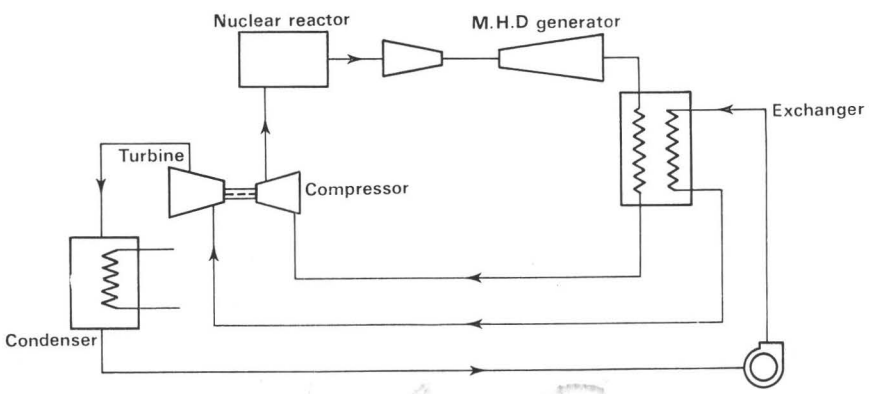

FIG. 3. — *Closed cycle MHD process* [2].

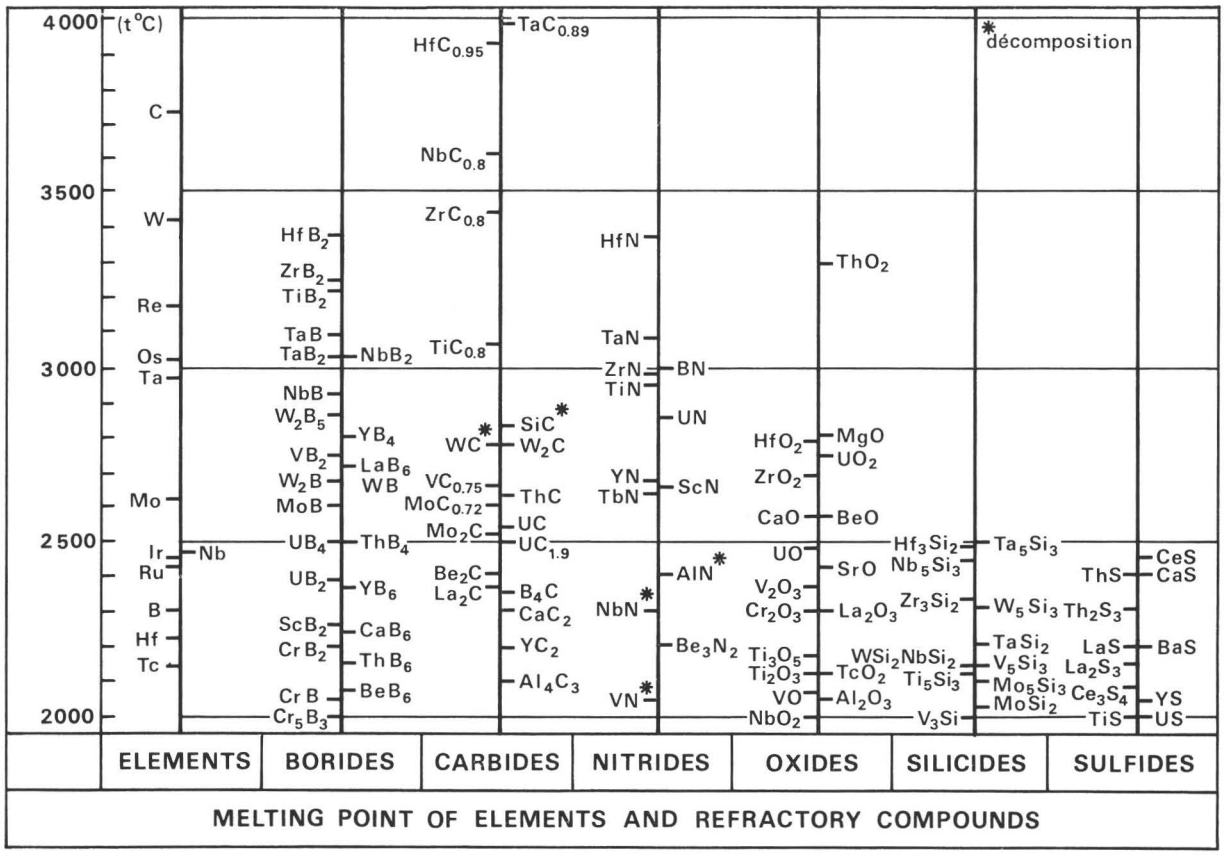

FIG. 4. — *Materials with melting point above 2,000° C* [3].

The properties required for the materials are:

— General:

High melting point (fig. 4) and low vapour pressure.
High resistance to abrasion from plasma jet.
High resistance to corrosion by insemination agents.
High resistance to oxidation: Boride, carbide and metals must not oxidize in the gas at high temperature.
High resistance to thermal shock.

— *For electrodes:* High electrical conductivity with high electronic transfer number even at low temperature.
High thermoelectronic emission at high temperature.

— *For insulating walls:* Low electrical conductivity. A material with all these properties does not exist. So, the choice is quite a difficult one. Insulating materials will be discussed first.

III. — INSULATING MATERIALS

We can see that all the oxides become conductive at high temperatures (fig. 5). The temperature dependence of σ requires that the temperature of the walls should not be higher than 1,500° C. The electrical resistance is between 10 and 10^3 Ωcm at the operation temperature. The materials possible are MgO, ThO_2, BeO, $MgAl_2O_4$ (spinel), zirconate and yttria.

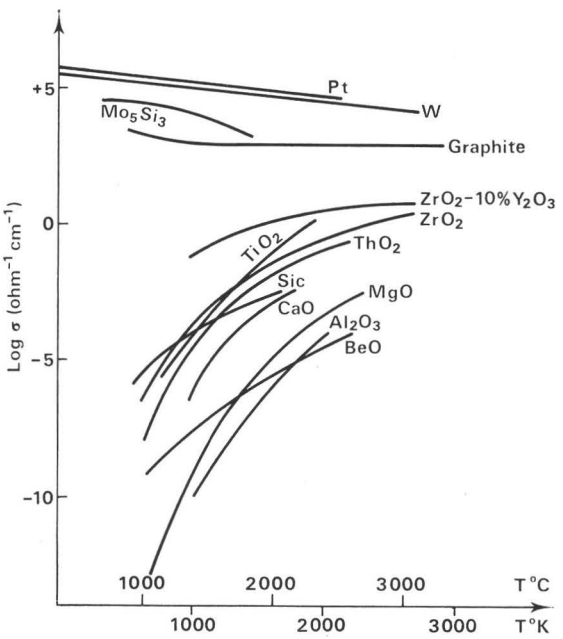

FIG. 5. — *Electrical conductivity of refractories oxides* [4].

A) Compounds

ThO_2 (T_F = 3,200° C) has the highest melting point among the oxides, high refractoriness and good resistance to corrosion. Good insulating but radioactive materials and high cost. No real application.

MgO is still stable at 2,300° C, which makes for a very good insulating material. This material is often used for MHD conversion. The performance of MgO depends on the purity. It seems that more than 2 % of Fe_2O_3, CaO and SiO_2 are not convenient. 2 MgO, SiO_2: forsterite, CaO, MgO SiO_2: monticellite, MgO, Fe_2O_3: magnesia ferrite are formed in grain boundaries which have poor corrosion resistance to alkalines. A good result is obtained by using compact blocks from electrically fused magnesia. The deterioration in insulation of electrically fused magnesia due to penetration of seed materials is considerably less than others since the magnesia block is very dense and has no open pores. These blocks are made so that the ⟨ 110 ⟩ direction of the periclase is parallel to the direction of the plasma flux. The weakness of MgO is its volatility. It is difficult to use at more than 1,500° C. It reacts with ZrO_2 or ZrB_2 electrodes.

Al_2O_3 (T_F = 2,040° C) is a very refractory material. Very attractive properties are its good mechanical resistance, its corrosion resistance, thermal and chemical stability and high electrical resistance. Unfortunately, Al_2O_3 reacts with K^+ to give some aluminates called βAl_2O_3, which are ionic superconductors. This oxide is more useful for the cold wall. A possibility is to arrange an MgO wall upstream of the Al_2O_3 wall, so that MgO volatilizes and forms with Al_2O_3 a spinel with good resistance to K^+.

BeO (T_F = 2,600° C) has a thermal conductivity similar to metals. It has a high resistance to thermal shock. Electrical resistivity is high. The problem of BeO is the toxicity, and this material can be used only for the cold system.

Zirconate MO, ZrO_2 [6]. $SrZrO_3$ (T_F = 2,740° C) is a good electrical insulator, but compositions having good properties are only found in the narrow range at stoichiometric composition (fig. 6). Other zirconates are $CaZrO_3$ (T_F = 2,340° C), $BaZrO_3$ (T_F = 2,700° C), $SiZrO_4$ (T_F = 2,420° C).

B) Structure of walls

To prevent the corrosion by potassium, one needs to use dense materials, but such materials are weak with respect to fracture. The structure of hot insulating walls will therefore be built from metallic elements separated from each other by refractory ceramic layers. Cooling will be required for the insulating material. The temperature of the walls is 1,650° C to 1,700° C. To get this temperature at the face of a water cooled wall, the thickness of the material depends on the heat flow. For example:

TABLE II

System	Heat flow ($W.cm^{-2}$)	Thickness (mm)
Laboratory, 200 KW	6-7	35
Pilot plan, 8 MW	50	6/7
Plant, 500 MW	400	0,8/0,9

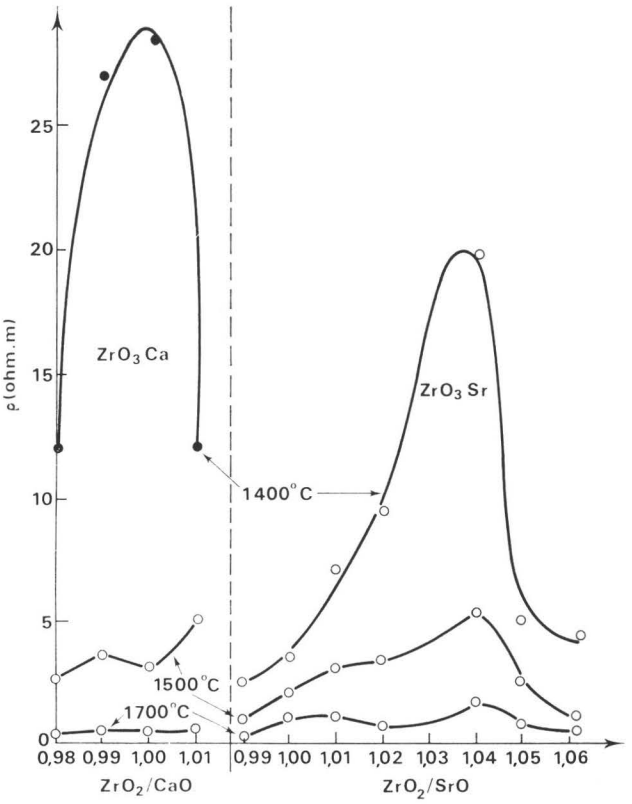

FIG. 6. — *Relation between the stoichiometry and the resistivity of insulators.*

The solution is the described wall structure and we can calculate the maximum size depending on the temperature of the front face. One uses some lamellae of MgO or $SrZrO_3$ joined by cement; the stainless steel prevents the migration of the potassium compound and assures the heat removal.

IV. — ELECTRODES

The cooling of walls may cause not only a large amount of heat loss but also many other undesirable phenomena such as the generation of arc spots which may cause serious damage to electrodes or a drop of potential of the electrodes which reduces the effective power. It may therefore be required to keep the temperature of the channel walls as high as possible. The following three material groups were selected as test materials for electrodes: Alloys, refractory metalloids and oxides.

A. — Metallic electrodes

Alloys have very good properties with respect to mechanical strength but very poor oxidation resistance. Many alloys were tested at 800° C [8]. The alloys belonging to the Ni — Cr group seem good but cannot be used at high temperatures. Some additions (Ta, Mo, Al_2O_3) improve the operating temperature but such electrodes are not promising at high temperatures (fig. 7).

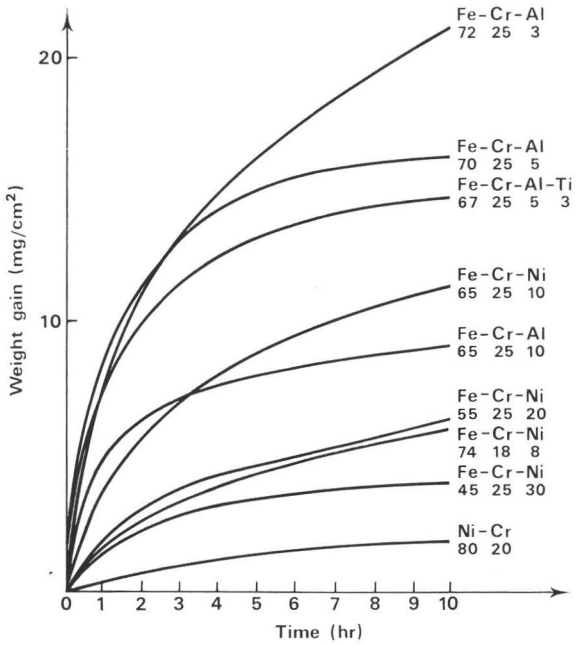

FIG. 7. — *Oxidation of high temperature alloys at 800º C in air* [8].

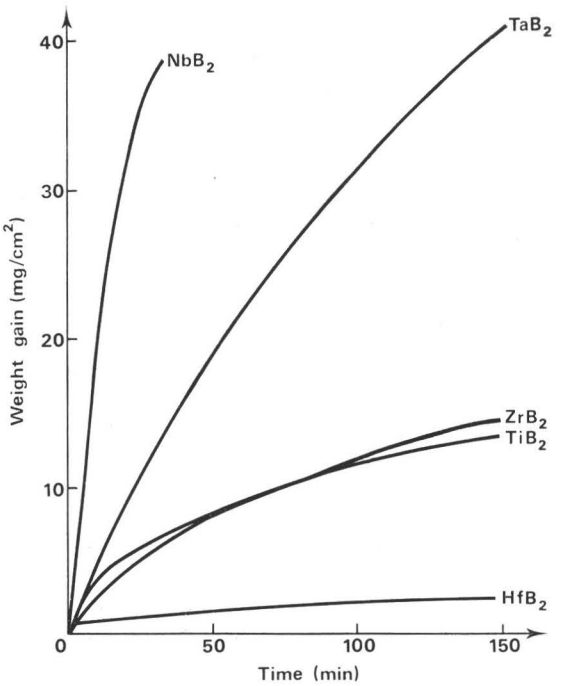

FIG. 8. — *Oxidation of selected borides at 1,330º C in air* [8].

B. — **Intermetallic ceramics**

Some carbides were tested: ZrC and SiC. SiC was tested in the Soviet Union at 1,500º C at a gas velocity of 500 ms^{-1}. It worked well for 50 hours but we have far to go to reach 10,000 hours. Oxidation was tested on several borides. HfB_2 and ZrB_2 are promising at 1,350º C (fig. 8). Their oxide films have a high melting point and considerably high conductivity at high temperature. Nevertheless the oxidation rate becomes large above 1,150º C with the activation energy changing from 35 kcal $mole^{-1}$ to 60 kcal $mole^{-1}$. 10 % $MoSi_2$ or BCr added to ZrB_2 improves the oxidation resistance.

It is important to obtain information on the processes on the electrode surface in order to develop materials for practical use. The preliminary test shows that when the lower electrode surface temperature was below 500º C, no electric current was observed up to an applied potential of 200 volts between the electrodes. At high temperatures of operation the current increases greatly [9]. For example, cobalt or niobium carbide give 15 to 20 A cm^{-2} under 200 volts, graphite only 7 A cm^{-2}. For a stable operation employing pure ZrB_2, it is necessary to keep the temperature of the electrode surface above 1,200º C.

C. — **Oxide ceramics**

ZrO_2 has a T_F of 2,700º C, but this material has a bad crystallographic transformation with some length change [4]. If one adds materials such as MO or M_2O_3, some oxygen vacancies appear and the cubic structure can be stable even at a low temperature: It is called stabilized zirconia. The best stabilizer is CaO or Y_2O_3:

$$Zr^{4+}_{1-x}Ca^{2+}_{x}O^{2}_{2-x}\square_x$$

$$Zr^{4+}_{1-2x}Y^{3+}_{2x}O^{2}_{2-x}\square_x$$

This material has good chemical inertness, low vapour pressure (10^{-6} bar at 1,700º C), a dissociation pressure of 10^{-12} bar at 1,700º C and very good electrical conductivity above 1,100º C. One problem of this material consists in its ionic conductivity. The assembly of current collector, electrode and plasma forms an electrochemical cell with the ionic material as the electrolyte. At the anode there is an oxidation reaction and at the cathode there is a reduction reaction. At the cathode, the ceramic-to-metal contact becomes poorer in oxygen; many vacancies appear and the zirconia becomes black and friable. The electrode is destroyed. We can improve this electrode with some flow of O_2 or CO_2 near the electrode. Some attempts have been made to make electronically conducting zirconia with 30 % CeO_2, to obtain an electronic contribution. The couple Ce^{4+}/Ce^{3+} is the reason of this electronic contribution (70 %). Some studies were made with rare earth oxides [10]. Another problem of ZrO_2 is the low electrical conductivity below 1,000º C. Many solutions were tried; some with cermets such as ZrO_2-Inconel, and some using platinum, which is expensive. It is possible to insert some wires into the ceramic, but the technology is not easy. Thus ZrO_2 has two disadvantages: Ionic conductivity and low electrical conductivity below 1,000º C.

$LaCrO_3$ (T_F = 2,490º C) is a new material with very good electrical conductivity, which is electronic, even at low temperature. As $LaCrO_3$ has poor corrosion resistance to K_2SO_4, some composite materials were tested. Some excellent materials were (fig. 10):

69 % ZrO_2 — 12 % CeO_2 — 19 % CaO	70 weight-%
$La_{0,95}Ca_{0,05}CrO_3$	30 weight-%
B_2O_3	1 %

It was recognized that B_2O_3 not only functions effectively as a sintering accelerator but remarkably improves the electric conductivity.

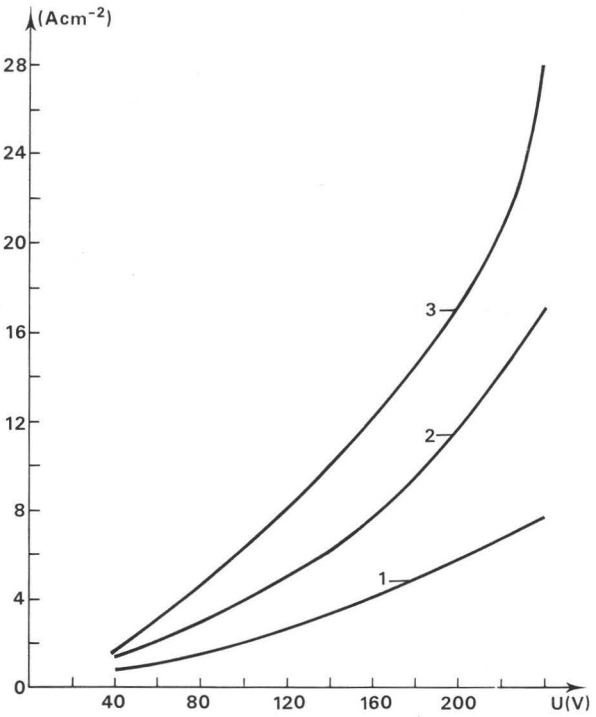

FIG. 9. — *Current/voltage relationship in hot electrodes. 1 graphite, 2 cobalt carbide, 3 niobium carbide* [9].

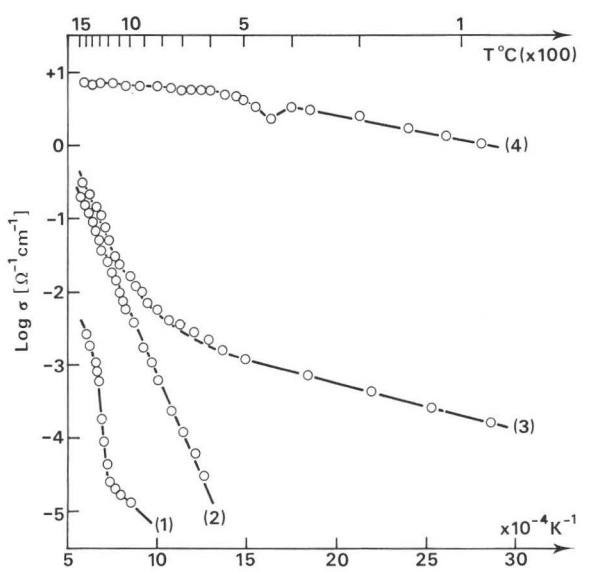

FIG. 10. — *Electrical conductivity of compounds with* $LaCrO_3$ [5]. [1] pure ZrO_2; [2] ZrO_2 — $LaCaCrO_3$; [3] ZrO_2 — $LaCaCrO_3$ — B_2O_3; [4] $LaCaCrO_3$ — B_2O_3.

The $LaCrO_3$ has poor corrosion resistance. Penetration of potassium into the electrode and loss of lanthanum and chromium from the ceramic are observed with both electrodes, but the former is more noticeable at the cathode and the latter more severe at the anode.

The temperature of electrodes must be near 1,700-1,800° C because of the vapour pressure of the materials, and they need to operate for 10,000 hours. Refractory oxide electrodes facing the plasma are backed by metallic conductors.

Some interesting results were obtained [11] on $FeAl_2O_4$ — Fe_3O_4 solid solutions. This is a totally electronically conducting material with a conductivity (at 1,600° C) of 1 mho cm^{-1} and without temperature dependance for 30 mole per cent of magnetite. By increase of additions the conductivity can increase to 200 mho cm^{-1}. The chemical stability features of the spinel electrode module were presented in [12] and the highest operating temperature is 1,780° C. The vapour pressure at these temperatures is less than 10^{-6} atm and tests without replenishment are possible for several hundred hours.

CONCLUSION

Since hot channel MHD operation tests do not yet reach the 1,000 hours life limit (table III), there is still a long distance to go before a continuous operation of the order of 10,000 hours can be achieved, which would make the practical use of MHD convertors possible.

TABLE III

Electrode material	Metals	Intermetallic	Oxides	MHD requirement
Life	10 h	100 h	1,000 h	10,000 h

Nevertheless, the great quantity of research done in this field has yielded a considerable spin-off for other applications. Practical examples are the development of ZrO_2 and $LaCrO_3$ high temperature heating elements for furnaces operating with oxidizing atmospheres, which was based on research on the electrical conductivity of these materials carried out in connection with their use for MHD generation; or the use of the ionic conductivity of ZrO_2 as a principle upon which the development of an oxygen gauging technique could be based.

* * *

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Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 237-249

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HIGH TEMPERATURE MATERIALS PROBLEMS IN FUSION REACTORS

By

J. BRESSERS (*) and W. VAN WITZENBURG (**)

1. *INTRODUCTION*

Controlled thermonuclear fusion research, started in the early fifties, has reached the stage of conceptual design studies of fusion reactor power plants. The fusion concepts mostly considered in these design studies are the tokamak, mirror and theta-pinch concepts with an electromagnetic confinement scheme and the inertially confined laser-pellet concepts. An important difference between these concepts is their mode of operation, being steady-state in the tokamak and mirror concepts and pulsed in the case of the theta-pinch and laser-pellet concepts. Excellent review papers, describing current conceptual designs were recently published by Steiner [1] and Ribe [2].

Because of its high reaction rate at relatively low temperatures the D — T — Li fuel cycle is considered to be the most feasible for the first generation of controlled thermonuclear reactors (CTR). Deuterium and tritium are the reactants, whereas lithium is required for tritium generation. The energy extracted from a fusion reactor appears as heat, generated by neutrons, plasma radiation and charged particles in the first wall and blanket structures, and would be recovered by a thermal energy conversion system. In some concepts direct energy conversion of the charged particles in electrical energy is a possibility.

Although in many respects materials problems in fusion reactors are qualitatively similar to those met in fission reactors, the environment in the former is undoubtedly characterized by more severe working conditions.

High temperature materials are required as construction materials for the first wall and its supporting and cooling structure. Metals and alloys commonly quoted as possible structural materials in CTR applications are the refractory metals vanadium, niobium and molybdenum and their alloys such as Nb — Zr, V — Ti and TZM, nickel base alloys and austenitic stainless steels. Other materials considered are SAP (sintered aluminium product), silicon carbide and graphite.

High temperature materials will also be used as non-structural components in fusion reactors, insulating materials being an important example. Another area of application is in liners, limiters and divertors as well as in the recently proposed internal spectral shifter and energy convertors [3].

The spectral shifter would be placed between the plasma and the first wall and would consist of graphite or siliconcarbide, thus not only reducing plasma contamination problems and first wall erosion, but also softening the neutron spectrum, resulting in a longer lifetime of the first wall. It is obvious that the environment for these components is to a large extent similar as for the first wall structure. Their property requirements may however be somewhat alleviated due to their non-structural role. The properties required for the successful application of high-temperature materials in CTR's depend on the fusion reactor concept. Yet the bulk of the material problems is, at least to some degree, common to all of them.

It is the purpose of this paper to illustrate the high-temperature materials problems in fusion reactors as

implied by current conceptual designs of fusion power plants.

2. HIGH TEMPERATURE MATERIALS ENVIRONMENT IN FUSION REACTORS

To situate the high temperature materials problems in a CTR a short consideration of terms is useful.

Figure 1 represents a sectional view of a magnetically confined toroidal fusion reactor. The plasma is confined magnetically and separated from the first wall by a vacuum envelope.

The first wall plays the role of a vacuum seal to the plasma chamber and is surrounded by the blanket. The blanket is a rather complex structure and has a triple role:

1. Slowing down of neutrons, thus converting their kinetic energy to heat.
2. Shielding of the superconducting magnet structure from radiation and heat.
3. Breeding of one of the reactants, tritium, through n(Li, He)T reactions on lithium or lithium compounds present in the blanket as a fluid or as a solid.

Since roughly two thirds of the fusion energy is released as neutrons and the breeding blanket absorbs most of the neutron energy, this blanket necessitates a cooling system.

The breeding material itself can be used as a coolant (direct cycle) or a secondary coolant (potassium, helium gas) may be used to transport the heat generated in the blanket structure to a heat exchanger. The blanket is covered with a shield which further reduces neutron and γ-fluxes to a level acceptable for the magnet structure. This shield may be composed of borated water, iron and a lead cladding contained within the main structure. The superconducting windings nessary to induce magnetic fields for the plasma containment and eventual plasma heating, are located outside the magnet shield [4].

The neutron energy spectrum at the first wall of a CTR is significantly harder than that in the core of fission reactors as a result of the 14.1 MeV neutrons generated in the D-T reaction. The uncollided neutron flux density at the first wall determines the « wall loading » which in most current conceptual designs is roughly 1 MW/m², corresponding to a neutron source strength of 4.4×10^{13} $n/cm^2.s$.

As a result of neutron scattering in the blanket the total time averaged fast neutron flux at the first wall is $\sim 3 \times 10^{14}$ $n/cm^2.s$. The first wall will also be exposed to a flux of mainly D, T and He ions and neutral particles escaping from the plasma and to plasma radiation. Total particle fluxes expected are of the order of 10^{13}-10^{14} particles/cm².s with mean energies ranging from 23-100 keV in tokamak systems to 0.3-2.0 MeV in the laser-pellet reactor model.

The energy deposition at the first wall and in the blanket of currently considered designs is pulsed, though for mirrors and tokamak devices the pulselength is of the order of 10^4 s. In theta-pinch systems the time dependent energy deposition is such as to cause temperature transients of $\sim 300°$ C in the first wall. In the laser-pellet concept the situation is even worse, since the energy is deposited at the first wall in 10^{-6} s or less, and the periodicity of the pulse is estimated to be ~ 1 s.

Non-uniformity in time will be aggravated by a non-uniformity in space of the energy deposition. Plasma charged particles for instance penetrate only some microns into the first wall. This non-uniformity in space results in thermal and neutron flux gradients giving rise to inhomogeneous stresses.

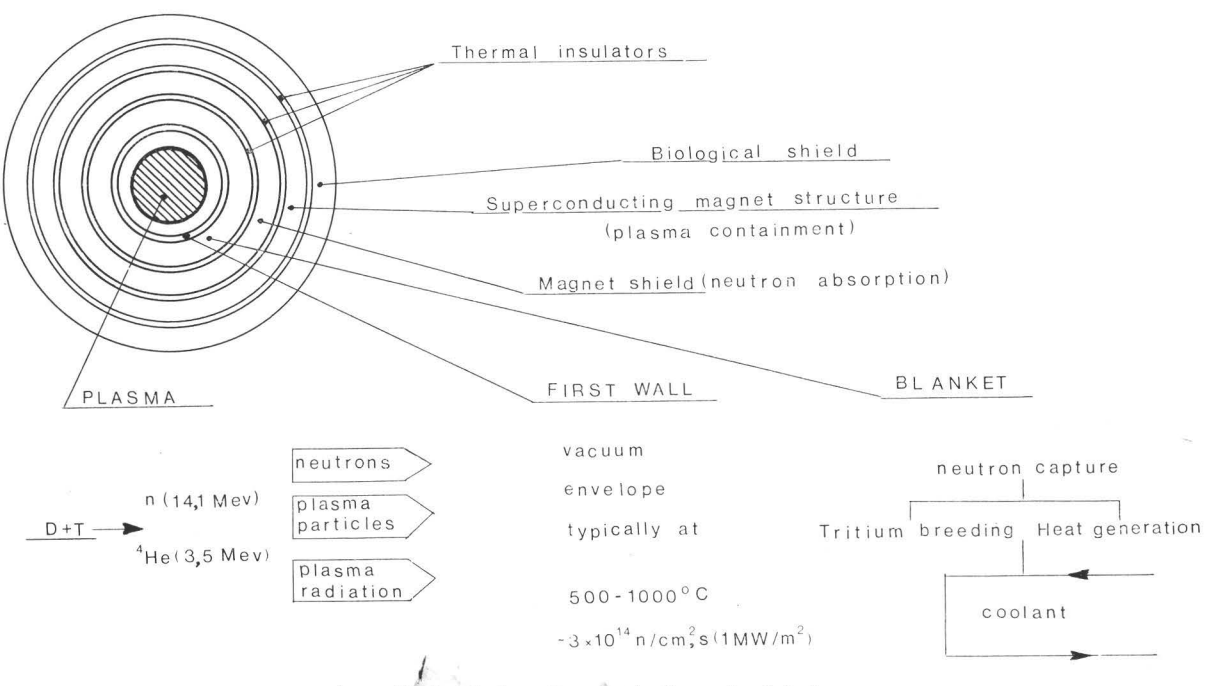

FIG. 1. — *Sectional view of magnetically confined fusion reactor.*

Operation temperatures of the first wall in current conceptual designs using stainless steel will be in the range 500-600° C. Designs in which refractory metals are considered are planned to operate at higher temperatures. Temperatures near 1,000° C may even be achieved in the longer term by using refractory metal based alloys.

Table I summarizes some of the parameters for current conceptual designs.

TABLE I

Concept	Tokamak	Mirror	θ-Pinch	Laser-Pellet
Confinement scheme	magnetic			inertial
	steady state		pulsed	
Neutron damage time (s)	10^3-10^4	> 10	10^{-1}	10^{-6}
Down time (s)	100-300	10^4-10^5	3-10	10^{-2}-1
Instantaneous wall loading (MW/m²)	1-5	1-5	30-500	10^4-10^6
Pulses/year	~ 5,000	~ 10	~ 3.10^6	~ 10^9

3. THE INFLUENCE OF RADIATION ON MATERIAL PROPERTIES

3.1. Basic neutron and ion induced phenomena

The primary effects induced by neutron and ion bombardment on high temperature structural materials in a CTR will now be considered.

3.1.1. **Displacement damage.** — Displacement of atoms from their equilibrium positions results in the production of self-interstitials and vacant lattice sites. These point defects interact mutually and with other lattice defects to form a damaged structure in the bulk of the target material [5].

It has become practice to express the quantity of irradiation in terms of displacements per atom (dpa) units *i. e.* the average number of times each atom in the sample has been displaced during the exposure. In table II, typical values for the number of dpa's to be expected in a CTR are compared to the values for the fission reactor EBR-II in a series of candidate materials for the first wall.

It appears that the displacement rate is relatively insensitive to the choice of the first wall material. It is also evident from this comparison that, at the neutron wall loadings of 1-3 MW/m², which are typical for current CTR designs, the overall defect production rates in the first wall of a CTR and in the core components of a typical fast reactor are of the same order of magnitude. Important differences, however, do exist. Instantaneous displacement rates are two to six orders of magnitude higher in pulsed systems. Moreover the neutron spectrum at the first wall of a CTR is much harder than in a fission reactor, resulting in a higher number of atomic displacements per neutron in the CTR case.

TABLE II. — *Atomic displacements for different first wall materials* [6].

	dpa/yr for 1 MW/m² in fusion reactor	dpa/yr (max) in EBR-II fission reactor
SAP	17	76
SS 316	10	44
Nb	7	28
Mo	8	30
V	12	54
C	10	5
Al_2O_3 [7]	15	

3.1.2. **Nuclear transmutation reactions.** — Transmutation reactions, caused by the incident neutrons, result in the production of gaseous and solid components in the matrix of the target material. As a result of the harder neutron spectrum in fusion reactors the transmutation rates in the structural materials subject to neutron radiation will generally be higher in fusion reactors than in fast fission reactors [8].

3.1.2.1. *Gaseous transmutation products.* — Table III lists literature values for He and H production rates in fusion reactor candidate materials. It is obvious from this table that the transmutation rate for He and H is one to two orders of magnitude higher for most fusion reactor structural materials than in the core of fast fission reactors. It is also evident from table III that, in contrast to the displacement rates, gas production rates depend strongly on the material.

TABLE III. — *Typical gas production rates.*

Material	Fusion reactor 1 MW/m²		Fast fission reactor EBR-II	
	appm He/yr	appm H/yr	appm He/yr	appm H/yr
Fe [9]	128	151	3	89
Ni [9]	28	570	72	1,568
Cr [9]	150	160	3	53
Nb [6]	24	79	1	6.6
V [6]	57	100	0.5	14
Mo [6]	47	95	1.8	3.5
C [6]	2,700	negligible	130	negligible
Be [6]	2,800	130 (T)	3,300	negligible
Nb-1 Zr [10]	29	76		
V-20 Ti [10]	53.5	181		
SS 316 [6]	200	540	4.7	270
PE 16 [11]	156	not reported		
SAP [6]	410	790	7.9	50
SiC [12]	1,800	575		
Al_2O_3 [7]	840	485		

3.1.2.2. *Non-gaseous transmutation products.* — Due to the hard neutron spectrum the generation of non-gaseous transmutation products in the first-wall and blanket structural parts will not be negligible. Some metals such as V (transmutation products Ti and Cr) experience only slight compositional changes. These changes become negligible in the case of the V-20 Ti first wall candidate alloy.

In other systems, however, transmutation reactions may cause quite important changes. In 316 stainless steel for instance, the Mn content changes from 2 at. % to ~ 6 at. % after 30 years of operation; in Nb the Zr content increases to ~ 6 at. % under similar conditions. The solubility limit of the transmutation product in the matrix material can thus easily be exceeded under appropriate conditions of wall loading and lifetime, resulting in second phase precipitation.

Another important aspect of transmutation reactions is the creation of radioactive nuclei in the irradiated materials, yielding problems in relation to afterheat at loss of coolant accidents and maintainance activities and to biological hazard and waste storage.

3.1.3. **Surface reactions.** — Surfaces of major components of CTR's, as structural first walls, divertor walls, collector electrodes of the direct convertor in the mirror reactor concept etc. will be exposed to a continuous impact of energetic particle fluxes and energetic radiation from the plasma. This results in wall erosion of these components due to processes like sputtering, blistering and evaporation and for tokamak and theta-pinches also in plasma contamination.

The energetic particles mainly responsible for the wall erosion processes are 14.1 MeV neutrons, hydrogen and its isotopes and helium in the form of neutrals, excited atoms or ions [13, 14].

The extent to which erosion phenomena occur depends on the reactor concept. The conditions are particularly severe in the inertial confinement systems where the first wall surfaces have to be covered with special ablative layers to avoid uncontrollable thermal stresses and evaporation processes as a result of the deposition of large quantaties of energy in very short times.

3.2. Radiation effects and their influence on material properties

The phenomena induced by plasma interaction with structural materials in a high-temperature environment of a CTR, which have been described briefly in the preceding sections, result in a number of effects. These radiation effects will be considered in the following sections, together with their influence on mechanical and physical properties of the high-temperature CTR candidate materials.

3.2.1. **Dimensional changes.** — There are two main causes of irradiation induced swelling occurring in metals in the temperature range of interest for CTR's.

Voids: $\sim 0.2\ T_m$ — $\sim 0.55\ T_m$ (T_m : melting point in K).

Bubbles: $\geq 0.5\ T_m$.

3.2.1.1. *Void swelling.* — Our knowledge concerning voids is largely empirical and emerges from fission reactor development programmes. The experimental results that have contributed to the understanding of elevated temperature irradiation damage have been highlighted recently by Eyre [15]. Voids result from the accumulation of vacancies into three-dimensional cavities and the preferential drift of self-interstitials to edge dislocations [16, 17]. Void growth is accompanied and influenced by the additional growth of interstitial edge dislocation loops into a three-dimensional dislocation network.

It has been suggested that voids nucleate at impurity atoms (metallic as well as non-metallic), at gas bubbles, or homogeneously. It is believed that the helium atoms generated by (n, α)-reactions play a critical role in both nucleation and stabilization of voids. An example of the influence of He on voidage is seen in figure 2 showing pure vanadium samples without and with 10 ppm He, both irradiated to 1.6×10^{21} n/cm^2 ($E > 0.1$ MeV) at 600° C. Swelling values $\Delta V/V$ are ~ 0.1 % and ~ 3.5 % respectively [18].

Swelling due to voids has been observed in the temperature range from $\sim 0.2\ T_m$ to $\sim 0.55\ T_m$ with a maximum around $0.45\ T_m$. The general experience is that void concentration decreases with increasing temperature whereas the average size increases. Both void density and void size depend on the metal, and its chemical composition and metallurgical state. A dose threshold for swelling in metals exists which varies with the type of metal purity and temperature, the lowest value being $\sim 10^{19}$ n/cm^2, which applies to aluminium.

Some metals do not swell even after high neutron doses: Au and Ti do not show voids up to a fluence of 3×10^{21} n/cm^2 [16] and V — 20 Ti does not swell even up to dose levels of 3×10^{22} n/cm^2 [6]. Voids are not observed in Zr irradiated with electrons or heavy ions up to 60 dpa in the temperature range 350-500° C [19].

At a constant temperature of irradiation the void density is often observed to increase up to a certain dose and remaining constant thereafter, whereas the void size keeps increasing with dose. Very large swelling values have been reported *e. g.* 30 % in stainless steel 316 after proton irradiation up to 100 dpa at 500° C [20]. Fortunately however, swelling does not increase indefinitely. Saturation effects have been observed, limiting void growth. Several saturation mechanisms have been proposed among which the formation of a stable, three-dimensional void lattice is considered to play an important role.

The swelling vs. temperature curve is shifted towards higher temperatures the higher the displacement rate. Shifts of 100° C to 200° C have been observed for a change in the displacement rate from 10^{-6} dpa/s to 10^{-3} dpa/s [6]. The implications are obvious when considering the broad range of instantaneous displacement rates met in pulsed CTR's.

The influence of impurity atoms on the void swelling characteristics has already been noted. The presence of alloying elements and small amounts of interstitial

stitial impurities have been reported [23, 26]. Experimental evidence shows that void swelling can also be influenced by thermomechanical treatment; for example cold work generally reduces swelling [30].

In addition to the effects of uniform swelling the effect of swelling gradients, resulting from temperature and neutron flux gradients in the reactor systems, can become very troublesome from the constructional point of view. In conjunction with ductility problems, which may arise as a result of radiation and helium embrittlement, differential swelling may impose unacceptable strain conditions.

3.2.1.2. *Gas bubble swelling.* — Gas bubble swelling is caused by the coalescence of helium gas atoms, introduced into the lattice as a result of (n, α) transmutation reactions and of radioactive decay of tritium. Tritium from the plasma and from the tritium breeding reactions occurring in the blanket diffuses into the structural materials and may build up to quite important concentrations in those materials in which hydrogen isotopes dissolve.

In Nb and V for instance, at an ambient pressure of 10^{-6} torr of tritium and at a temperature of less than about 200° C the generation of helium from tritium decay exceeds that from (n, α) reactions.

A similar situation might even develop in those metals like Mo which normally do not dissolve hydrogen, but which do very much so in a radiation damaged condition as a result of trapping of hydrogen atoms at defects.

Thermal release of helium atoms out of the structural candidate materials for CTR's is not expected to occur below temperatures of about 1,100-1,200 K [31] due to trapping of helium by radiation defects.

Helium gas bubble formation will start at temperatures $\geq 0.5\ T_m$ where the helium atoms become sufficiently mobile. Because the average bubble size is unlikely to exceed 1,000 Å the amount of swelling is expected to be within the 1-10 % range for the helium gas concentrations generated in CTR high-temperature components [32]. Figure 3 is an example of helium gas bubbles in vanadium, after injection of 1,000 appm helium at 750° C [33].

3.2.1.3. *Swelling in non-metallic materials.* — Swelling in SiC and carbon materials has been extensively investigated under fission reactor conditions. The swelling

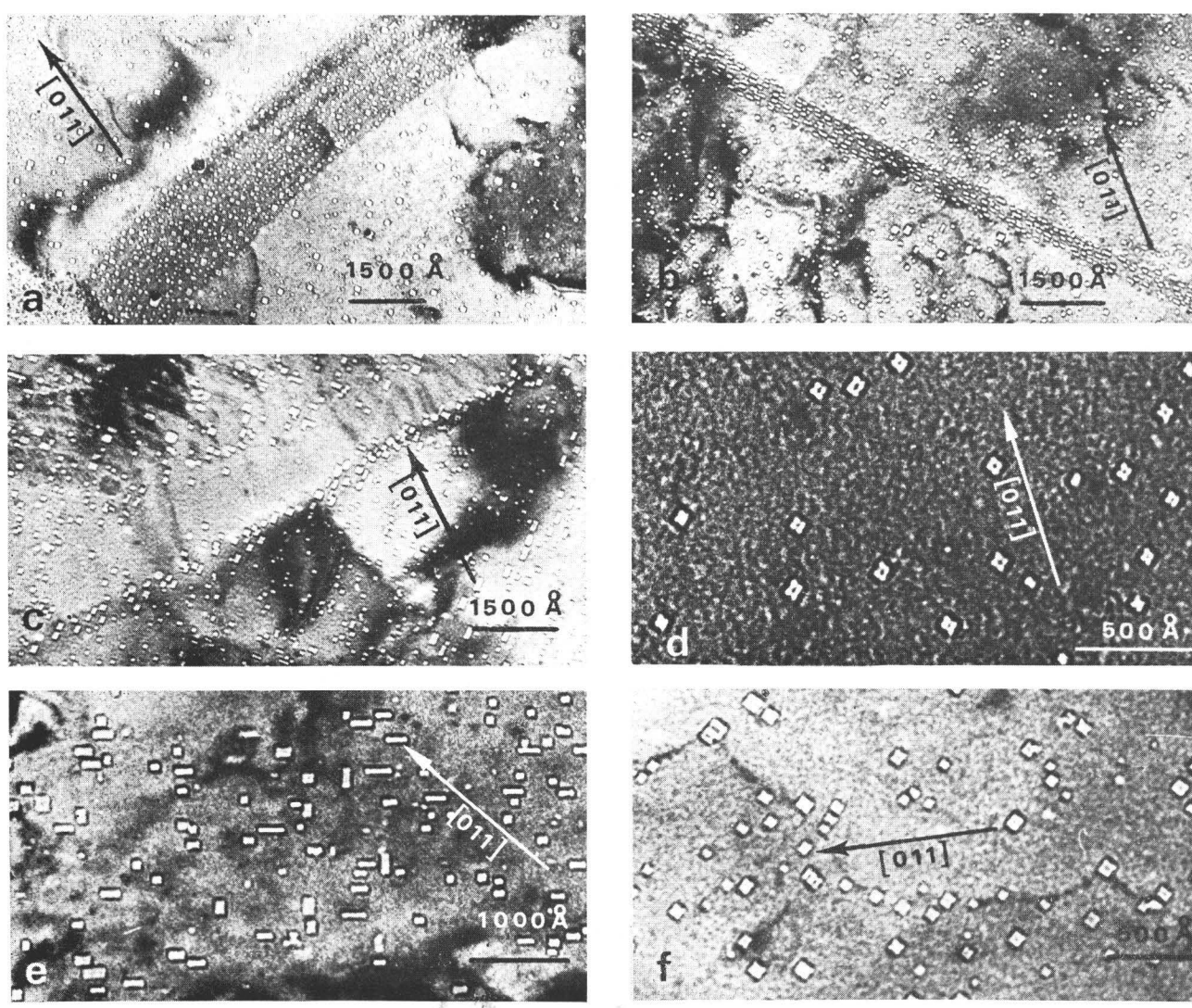

FIG. 3. — *Heterogeneous distribution of helium gas bubbles in V. Helium implanted to 1,000 appm He at 750° C.*

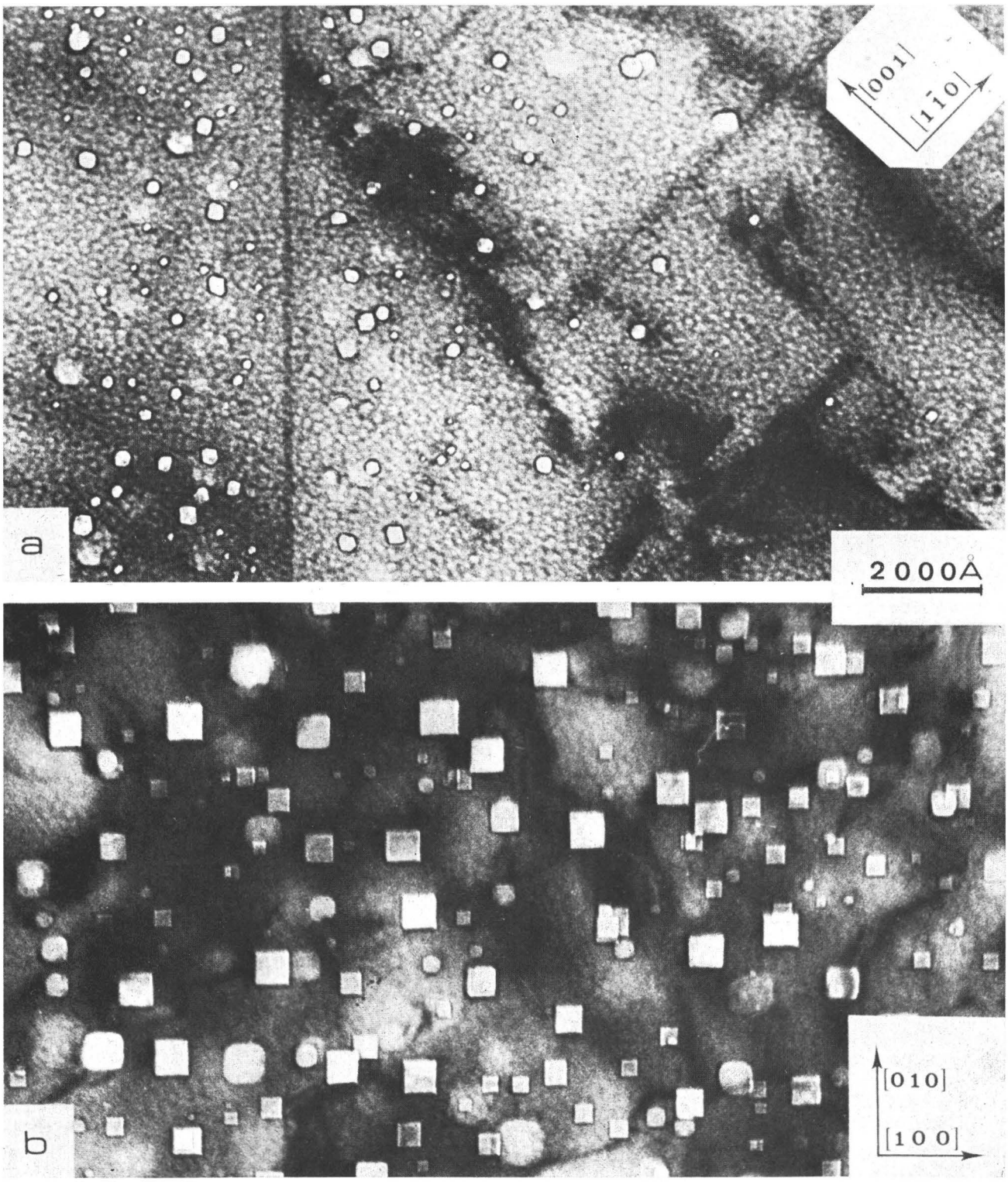

FIG. 2. — *Pure V irradiated to 1.6 × 10^{21} n/cm² (E > 0.1 MeV) at 600° C :* (a) *without He;* (b) *with 10 appm He preinjected on a cyclotron at ~ 250° C.*

impurities can appreciably alter the swelling. Alloying Ti and Zr to Mo (TZM) reduces swelling to negligible amounts even when irradiated up to $\sim 8 \times 10^{22}$ n/cm^2 (E > 0.1 MeV) [21]. Similar results were reported on alloys of Zr in Nb [22, 23] and of Ti in V, though an increase in swelling was also observed upon alloying Zr to Nb [24, 25]. These examples merely serve to demonstrate the contradictory observations often reported.

Generally, however, it appears that oversized solute atoms suppress radiation induced void swelling [26].

The situation is also not very clear with regard to the influence of interstitial impurities on swelling characteristics. Reduction of void swelling due to interstitial non-gaseous impurities (C, possibly Si) has been observed on a number of occasions [27, 28. 29]. Both enhancement and reduction of swelling due to gaseous inter-

mechanism is fairly well understood. In most cases the starting material is not 100 % dense. Neutron generated point defects cause densification by filling up micro-posities. Further irradiation leads to a « break away swelling » phenomenon which can result in very severe distortions. In general, carbon may be useful up to neutron fluences of 10^{22} n/cm^2 (fission spectrum) whereas in SiC in the neighbourhood of 1,000° C only limited swelling is observed up to fluences of 10^{23} n/cm^2 [5, 12].

Swelling has been observed also in insulating materials. Al_2O_3 was observed to swell up to 3 % after neutron irradiation to 6×10^{21} n/cm^2 ($E > 0.1$ MeV) in the temperature range 375° C-750° C whereas Y_2O_3 did not swell under similar conditions [34]. Experimental data on swelling in insulators are, however, scarce.

3.2.2. **Effects on mechanical properties.** — Neutron irradiation induced atomic displacements and transmutations, especially those producing helium and to a lesser degree also hydrogen, will affect mechanical properties of metallic and non-metallic materials.

3.2.2.1. *Strength and ductility.* — In general metals exposed to neutron irradiation will exhibit an increase in strength (radiation hardening) and a decrease in ductility (radiation embrittlement). The magnitude of these effects and the fracture mechanism depend on the irradiation and/or test temperature because of their influence on the type, size and concentration of the defects. Irradiation conditions producing an increased matrix strength for instance due to point-defect clusters lead to low temperature embrittlement. At temperatures well below 0.5 T_m fracture is likely to occur transgranularly preceded by deformation in limited zones (channels) in which the first moving dislocations sweep up the irradiation produced point defect clusters. At temperatures approaching 0.5 T_m the tendency of wedge-crack formation at grain-boundaries and of cracks to propagate along grain-boundaries increases, leading to low ductility intergranular fracture.

For both bcc and fcc metals the low temperature embrittlement will be directly dependent on the number density of point defect clusters, which form obstacles to dislocation motion. However, indications are that for bcc metals the irradiation hardening mechanism is complicated due to interaction of interstitial impurity atoms (C, O, N) with the point defect clusters [35].

Interstitial impurities are also influencing the ductile-brittle transition temperature (DBTT) in bcc metals which is characterized by a change in fracture mechanism from shear (ductile behaviour) above this temperature to cleavage (brittle behaviour) at lower temperatures. Experimental evidence shows that neutron irradiation increases the DBTT. After irradiation at 100° C to 5×10^{19} n/cm^2 the DBTT of stress relieved molybdenum increased from — 136 to — 70° C. For fully recrystallized tungsten only a minor increase was observed [36]. Since the DBTT is not a material constant, but does depend on strain rate and structural variables as for instance grain-size, these figures have only qualitative significance. However, it should not be ruled out at present that at higher fluence levels the DBTT could be so high that on cooling of a Mo or W first wall from operating to room temperature, thermal stresses may cause collapse of the structure.

With increasing temperature irradiation hardening due to displacement damage decreases because of annealing of the point-defect clusters and also because of the ability of dislocations to surmount irradiation produced obstacle (*e. g.* by climb). At temperatures above 0.5 T_m another embrittlement mechanism takes over: high temperature embrittlement, which leads to grain-boundary failure by cavitation, usually without affecting the strength significantly [37].

The major cause of high temperature embrittlement is the production of helium by (n, α) reactions. At high temperatures helium aggregates in bubbles at grain-boundaries, leading to enhancement of intergranular fracture (fig. 4). The loss of ductility becomes progressively worse with increasing test temperature and helium concentration. The reduction of ductility with increasing helium concentration is of particular importance in CTR's because of the large helium production rates (see table III).

Bloom and Wiffen [39] have recently investigated the effect of large helium concentrations on the mechanical properties of neutron irradiated 316 between 400 and 800° C.

Helium concentrations up to 6,000 appm were investigated and were observed to considerably reduce the ductility as well as the mechanical strength. Bloom and Wiffen judge the degradation of mechanical properties of 316 under CTR conditions to be unacceptable above 550° C.

That helium at far lower concentrations can seriously reduce the ductility of the fcc iron and nickel base alloys at test temperatures above ~ 0.4 to 0.5 T_m has been demonstrated extensively [39]. Even helium concentrations as low as 10-20 appm lead to ductility losses of over 80 % at temperatures above 600° C.

Indications are that bcc metals and alloys are less sensitive to helium embrittlement. Helium concentrations up to 10 appm do not affect the ductility at high temperature of vanadium and vanadium-alloys [40, 41]. The ductility of TZM is still unaffected at 20 appm [37]. At higher helium concentrations, up to about 100 appm, some reduction of the uniform and total elongation has been observed for vanadium, niobium and their alloys [42, 37]. At even higher helium concentrations, up to 500 appm in niobium, the decrease in ductility is accompanied by helium induced grain-boundary decohesion [43].

Hydrogen and its isotopes, resulting from (n, p) reactions and present in the blanket as well, may also seriously affect the mechanical properties of structural materials. The solubility and diffusivity, which determine to a large extent the magnitude of their influence on mechanical properties, is not expected to be very isotope dependent [44]. Molybdenum does not form

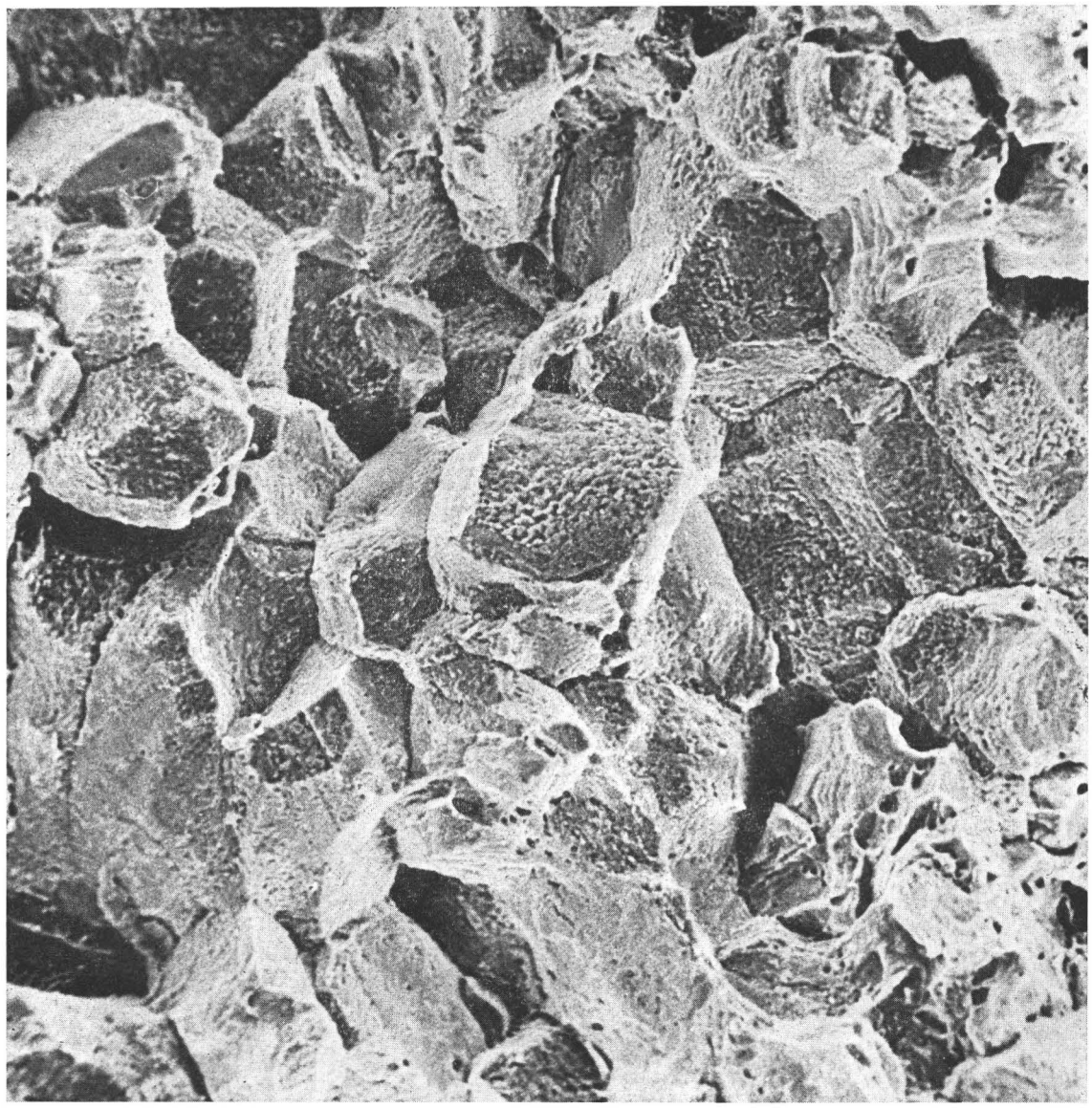

FIG. 4. — *Intercrystalline fracture surface of 316 stainless steel sample irradiated at 500° C to a fast fluence of 3 × 10²⁰ n/cm² (E > 0.1 MeV, 10 appm He) and creep tested at 600° C* (Magnification 300 ×).

hydrides and has a very low hydrogen solubility even at high temperatures. In niobium and vanadium, having a somewhat larger solubility, stable hydrides are formed near room temperature. As a consequence molybdenum is not embrittled while niobium and vanadium are significantly embrittled by hydrogen at concentrations of the order of 1,000 appm near room temperature [45, 46]. Stable austenitic stainless steels do not appear to be embrittled by hydrogen at room temperature [44]. Virtually no experimental information is available concerning hydrogen embrittlement at high temperatures. It has been suggested that because of the resistance of stable austenitic steels and molybdenum to hydrogen embrittlement at low temperatures, these metals should also not be embrittled by hydrogen at CTR working temperatures.

Non-gaseous transmutation products, interacting with irradiation produced defects, could also influence mechanical properties. For example, Nb and Nb-1 Zr, neutron irradiated to ~ 30 dpa and tested at temperatures near 450° C had a uniform elongation of 10 % and 0.1 % respectively [22]. Clearly the transmutation of niobium into zirconium, which is significant in a CTR environment, will contribute to embrittlement.

Strength and ductility of ceramics are normally not significantly affected by neutron doses up to ~ 10^{20} n/cm^2. Above this level irradiation can lead to a catastrophic loss of mechanical strength as is evidenced by the behaviour of alumina fracturing without any external load being applied after irradiation to 5×10^{21} n/cm^2 in the range 600-1,000° C [47].

The mechanical properties of siliconcarbide and pyrocarbon, depending on the method of fabrication and resulting microstructure, are considered to be in a range suitable for structural applications in CTR's [12]. The main difficulty with these materials is the small strain to fracture.

3.2.2.2. *Creep and fatigue.* — Ductility and strength are usually evaluated by means of simple short duration tensile tests. However, because of the magnitude of the

stresses to be imposed on the first wall and blanket structures (estimated to be in the range of 10-1,000 N/mm² [48], which are also cyclic in nature, creep and fatigue most likely will control the life of these structures.

Thermal creep occurs by grain deformation and grain-boundary sliding, the ratio of these two mechanisms being dependent on the microstructure of the material, its temperature and the applied load. Although diffusion is rate controlling during high temperature creep, grain-boundary cohesion and matrix strength obviously will influence the rupture life. That the relation between strength and ductility on one hand and creep rate on the other is not a simple one is clear from the fact that irradiation can reduce or increase the post-irradiation creep rate or leave it unaffected.

Metallic and non-metallic materials will exhibit an increase of creep-rate during neutron irradiation. This process, which for metals occurs between 0.3 and 0.5 T_m, decreasing exponentially with increasing temperature in this range, is called radiation creep [49]. This effect is not entirely understood yet, but must be related to irradiation produced vacancies and interstitials [50]. The supersaturation of these point defects will assist dislocations to overcome obstacles to slip by climb [51]. Radiation creep does not depend on thermal activation. Its rate depends on neutron flux, the stress (linearly) and the microstructure of the material.

No experimental information appears to be available concerning radiation creep at high temperatures of bcc metals. Moteff [49] assumes that irradiation creep in these metals should occur in the same homologous temperature range as observed for fcc metals. The magnitude of radiation creep, as suggested by experimental evidence on fcc metals, is such that under CTR operating conditions it may well be the dominant deformation mode.

Radiation creep of graphite, for which experimental data exist, apparently deviates from metals in its irradiation temperature dependence. Radiation creep of widely different graphites has been found to increase with temperature in the range 400-1,500° C during fast neutron irradiation at flux levels of $\sim 0.2\text{-}2.5 \times 10^{14}$/cm².s [52]. Radiation induced creep for SiC is very small compared to graphite [12].

Fatigue consists of crack nucleation followed by crack growth. Crack nucleation during fatigue tests will generally be accelerated by neutron irradiation. The crack propagation rate could be affected both positively and negatively even in one material after the same fast fluence but tested at different temperatures [53]. Neutron irradiation produced changes in fatigue properties are also attributed to either displacement damage or helium generated by transmutation reactions. At lower temperature (*e. g.* $\sim$ 500° C for stainless steel) an improvement in fatigue crack growth rate may result from displacement damage. Displacement damage usually raises yield strength and lowers ductility, both of which tend to reduce the size of the plastic zone at the crack tip and in turn reduce the crack growth rate. At higher temperatures ($\sim$ 600° C for stainless steel) displacement damage will largely anneal out. Helium may cause a decrease in crack growth resistance. A mechanism leading to the opposite effect would be helium impeding dislocation motion by pinning or dragging. This mechanism could explain the experimentally determined doubling of fatigue life at 900° C of TZM by helium injection to 10 appm [54].

The influence of hydrogen and its isotopes on creep and fatigue properties appears to be detrimental [45].

3.2.3. **Surface erosion effects.** — Surface effects are important from two points of view [1]:

— plasma contamination by impurities originating from surfaces exposed to plasma radiation, resulting in plasma energy and particle losses. These must be minimized in order to achieve adequate heating of magnetically confined plasmas;

— erosion of the wall surfaces in the environment of the plasma, leading to a reduced lifetime of components such as first wall, divertors in tokamaks, etc.

Surface erosion of the solid walls facing the plasma mainly results from two processes, termed sputtering and blistering.

Since the experimental evidence related to sputtering and blistering under CTR conditions is limited and the magnitude of plasma particle fluxes is uncertain, wall erosion rates are difficult to estimate. However, wall erosion is considered to be a problem and in order to reduce wall erosion and plasma contamination several techniques have been proposed including tailoring of the plasma particle streams through diversion of charged particles to collector plates or the use of sacrificial low Z walls in tokamak type reactors (liners) [14].

3.2.3.1. *Sputtering.* — Energetic neutral or charged particles striking the surface of a solid with energies larger than a threshold value (20-100 eV) may lead to ejection of surface atoms, termed physical sputtering. The efficiency of the process is determined by the sputtering yield *i. e.* the mean number of target atoms ejected per incident particle. Sputtering yields differ widely from metal to metal. For 20 keV D^+ bombardment the sputtering yield for Nb, being $\sim 10^{-3}$ atoms/ion, is an order of magnitude less than for Mo and stainless steel 316. Experimentally it has been observed that sputtering yields are nearly independent of the target temperature for temperatures $T \leq 0.7\ T_m$. For $T > 0.7\ T_m$ the yields increase nearly exponentially.

Surface structure and the presence of adsorbed layers are factors influencing the sputtering yield.

The dependence of sputtering yield on angle of incidence θ of the bombarding particles seems to obey a $1/\cos\theta$ law, at least for light ions [55, 56].

The energy dependence of the sputtering yield goes through a maximum which for niobium lies in the range 1-10 keV. The sputtering yield increases rapidly, as the mass of the incident particle approaches that of the target atoms, so the second order effect of self-ion sputtering may be significant. Insulators behave similarly as metals as far as sputtering due to plasma-particles is concerned, sputtering yields being generally somewhat lower. In contrast to metals, however, sputtering of insulators increases rather strongly with increasing temperature [55, 57].

Besides plasma-particle sputtering also fast neutron sputtering is a reason for concern. The neutron flux in a CTR will be composed of source neutrons (14.1 MeV) and of lower energy neutrons originating from back-scattering and nuclear reactions of high energy neutrons in the blanket region.

Although the neutron energy spectrum expected in a CTR can be reliably calculated, the sputtering yields for fast neutrons (> 10 MeV) on CTR candidate materials are an area of considerable controversy. Experiments and calculations point to sputtering yields of the order of 10^{-3} to 10^{-4} atoms ejected per incident neutron [55].

An additional phenomenon called « chunk ejection » has been observed to occur under 14 MeV neutron bombardment [14, 57]. The larger fraction of material sputtered under 14 MeV neutron bombardment is in the form of chunks consisting of some 10^{12} to 10^{13} atoms, resulting in sputtering yield values of 0.25 atoms/neutron and to an erosion rate of $\sim$ 0.1 mm/year at 1 MW/m^2 as a result of source neutrons. Chunk emission is attributed to stored energy in the crystal surface (*e. g.* due to cold rolling) and to the surface microstructure (micro-protrusions, microcracks). Chunk ejection was observed to be eliminated if the tensile stresses in near surface regions are reduced and if the surface smoothness is improved.

3.2.3.2. *Blistering.* — Blisters are aggregates of gas particles just below the surface of a solid wall. Gaseous particles originating from the plasma, charged as well as neutral, continuously strike the walls facing the plasma and penetrate the surface. In the region of intense damage near the end of the particle range the gas atoms can be trapped by the radiation induced vacancy point defects. As a result gases like helium, which are almost insoluble in metals but which have been shown to diffuse very well in metal lattices at elevated temperatures may become trapped in metals in large quantaties and may form stable bubbles [56, 58].

Such bubbles near the surface region can grow and form visible blisters when the gas pressure in the bubble is large enough to deform the surface skin. Eventual rupture of these blisters leads to gas release that may contaminate the plasma and the peeling off of the blister skin results in wall erosion.

Blistering has been observed over the energy range $\sim$ 10-2,000 keV for helium and other inert gases as well as for hydrogen and its isotopes in metals in which they are not soluble.

Blister formation is not observed until a critical dose is reached, the value of which depends on several variables, including irradiation temperature and energy. Critical doses are $\sim 10^{17}$ to $\sim 10^{18}$ particles/cm^2 for helium bombardment and $\sim 10^{18}$ to $\sim 10^{19}$ particles/cm^2 for hydrogen bombardment over a wide range of temperatures and energies [1]. Blister size, shape and density depend on a large number of parameters including incident particle parameters (energy, angle of incidence, dose rate, dose) and target parameters (temperature, yield strength, mobility of bombarding particles in the lattice, initial defect concentration of the solid, etc.) [59].

The erosion rate is strongly dependent on target temperature, increasing with temperature until a maximum is reached and then decreasing. The increasing gas pressure in the blisters and the decreasing yield strength with increasing target temperature are responsable for the maximum. The further decrease is believed to be related to helium release through either atom diffusion or migration of small bubbles [14].

Reported evidence suggests that erosion due to helium blistering in a CTR could be a more effective surface erosion process than physical sputtering by deuterons, tritons and helium ions for comparable energy ranges. However, it is quite possible that on surfaces bombarded with helium ions having a broad energy and angular distribution spectrum (which are conditions to be expected in a CTR) blistering may be completely avoided [60].

3.2.4. **Neutron-induced activity.** — In CTR systems two main sources of radioactivity exist [1, 6] :

— tritium necessary as a reactant in D-T fuelled systems. Since tritium, being an isotope of hydrogen, has a rather high permeability in many materials, high-temperature materials problems do exist in connection with the containment of tritium,

— reactor components activated by neutron bombardment. Radioactivity due to such components grows during reactor operation and reaches a significant fraction of its steady-state level after a period of the order of a year. The activation of the structure at equilibrium generally will be of the order of $\sim$0.4-4 Ci/W of reactor thermal power for a wide range of materials, blanket designs and neutron wall loadings (1-10 W/m^2).

From the technological (operation and maintenance activities) and safety (loss-of-coolant accidents, radioactive waste problems) points of view afterheat and biological hazard and their time dependent behaviour are of more concern.

Since neutron-induced activity is linked directly to the element irradiated, alloying elements as well as impurities present in structural materials may influence significantly the afterheat and biological hazard.

3.2.4.1. *Afterheat.* — In the absence of cooling the temperature of the activated first wall and blanket structure will rise due to nuclear decay. The maximum afterheat power density usually occurs in the first wall and varies almost linearly with neutron wall loading. Normalized to a 1 MW/m^2 neutron wall loading the afterheat power density of the first wall is of the order of $\sim$ 0.5-1.0 W/cm^2 at shutdown, *i. e.* one to two orders of magnitude less then anticipated for fast breeder reactors [1]. In contrast to Nb based alloys other potential CTR materials like SiC show afterheat values dropping very rapidly after shutdown. In SAP and V structures similar quick drops would be observed. In both examples the afterheat within hours for SiC and within weeks for SAP and V would be controlled by impurities [1, 10, 61].

3.2.4.2. *Biological hazard potential (BHP).* — Generally the BHP associated with the activated high-temperature CTR structural materials envisaged today will be one to three orders of magnitude below that

associated with the plutonium isotopes in an advanced fission reactor.

In contrast to Nb-1 Zr structures which are characterized by long-time BHP's the vanadium BHP seems to offer less difficulties.

The BHP of Fe and Ni-base alloys is roughly comparable to that of Nb-base structures on time scales of 10 to 30 years.

The BHP of SiC will be controlled by impurity activation [1, 10, 61].

3.2.5. **Effects on physical properties.** — In addition to changes in mechanical properties, caused by neutron irradiation, also physical properties will be affected. Physical properties of prime importance in CTR application are thermal and electrical conductivity, thermal expansivity and elasticity coefficient.

For metals the changes of physical properties will generally be much smaller than those of mechanical properties. Ignoring the phononic component of the thermal conductivity, which for metals is small, one may expect on basis of the Wiedemann-Franz relation that the thermal and electrical conductivities of metals are affected identically by irradiation produced physical and chemical impurities. Point defect clusters may significantly contribute to electron scattering. However, at high temperatures, where most of the displacement damage will anneal out, only transmutation produced impurities are expected to reduce the conductivities. This reduction will certainly not be more than a few percent.

For ceramic materials, *e. g.* Al_2O_3 and Y_2O_3, changes in the thermal and electrical conductivities appear to be quite large. Measurements by Reichelt *et al.* [62] on high purity Al_2O_3 and Y_2O_3, irradiated in the EBR-II to $\sim 10^{22}$ n/cm^2 ($E > 0.1$ MeV) at $\sim$ 750° C, showed a reduction of the thermal conductivities at $\sim$ 700° C to about half their original values. The electrical conductivity of both oxides increased roughly two orders of magnitude [63].

The reduction in thermal conductivity of reactor-grade graphite is less the higher the irradiation temperature. Fast neutron irradiation up to $\sim 10^{22}$ n/cm^2 ($E > 0.1$ MeV) at 600° C decreased the room-temperature thermal conductivity roughly ten times compared to the unirradiated material, while for an irradiation temperature of 1,600° C the decrease is less than twice [64]. Irradiation defect clusters produced at lower temperatures appear to be more effective in reducing thermal conduction than those produced at higher temperatures. The electrical conductivity of graphite, though less affected, is also reduced upon irradiation. This reduction is largest for irradiation temperatures around 800° C-1,000° C [65]. The room-temperature electrical conductivity after irradiation at 500° C to fast fluence levels above 10^{21} n/cm^2 is roughly half the unirradiated value.

Experimental data concerning irradiation induced changes in the thermal expansion are virtually non-existent. Kircher and Bowman [66], drawing a parallel between the influence of cold work and irradiation on thermal expansivity, suggest that changes may be expected. However, again, at high temperature where irradiation damage is predominantly due to transmutation, it is unlikely that the thermal expansivity will be affected significantly. The same argument may be used for the elasticity modulus.

4. COMPATIBILITY

Heat removal from the first wall and blanket structures in current CTR concepts occurs by cooling with liquid lithium, lithium containing fluoride salts (*e. g.* Li_2BeF_4) or helium.

Corrosion resistance is strongly affected by impurities such as hydrogen and its isotopes, oxygen and carbon. These impurities originate from the plasma, from nuclear reactions and from outside sources.

4.1. Corrosion in liquid lithium

The corrosion resistance of the refractory metals and their alloys is promising when their oxygen content is sufficiently low. Under these conditions niobium and tantalum based alloys were observed to be hardly corroded when exposed to lithium near 1,200° C for periods of the order of a year [67, 68].

Vanadium and Mo-0.5 Ti were reported to be corrosion resistant at temperatures of about 850° C, the exposure times being around 1,000 hours [69].

In contrast to the behaviour in sodium, refractory metals are not corroded in lithium containing oxygen impurities [70, 71]. The presence of oxygen in refractory metals on the contrary can lead to lithium penetration and formation of complex oxide phases. The oxygen concentration threshold above which lithium attack occurs, depends on the metal, being roughly in the range of 1,000-2,000 appm for niobium and vanadium. Alloying additions increase the threshold oxygen concentration for lithium penetration.

The high solubility of nickel in liquid lithium will limit the use of stainless steels and nickel based alloys to temperatures below $\sim$ 500° C [69, 72].

Graphite does not appear to be compatible with liquid lithium [1]. The corrosion resistance of insulating materials strongly depends on the material, with Al_2O_3 not being corrosion resistant at 375° C, whereas insulators such as BeO, ThO_2 and Y_2O_3 are fairly inert [73].

4.2. Corrosion in lithium containing fluoride salts

As a result of tests in fission reactor programmes molten Li_2BeF_4 has been shown to be compatible with many structural metals and graphite. Molybdenum and its alloys are not very corrosion resistant whereas niobium and iron-base alloys would be suitable for operation up to temperatures in the range 600-700° C [74]. The corrosion effectiveness of fluoride salts under CTR conditions may however be enhanced as a result of magnetohydrodynamic effects. EMF's induced between the fluid and its container may lead to galvanic corrosion

4.3. Corrosion in helium

Helium being an inert gas is not corrosive. The « corrosive » character of a helium coolant is due to impurities, continuously introduced in the cooling medium from outside sources. In order to avoid interstitial contamination of niobium and vanadium based alloys during prolonged exposures at 600º C or above, residual impurities such as oxygen and moisture have to be maintained at concentration levels which are currently impossible to maintain in helium loop circuits (less than 1 ppb) [74]. Possible solutions to this problem are additions of gettering constituents. Molybdenum may be used in combination with helium cooling since it has been observed to be compatible with commercially pure helium up to ~ 1,000º C.

5. *CONCLUDING REMARKS*

The rate at which the mechanical properties and the dimensional stability of the first wall and blanket materials will be affected by neutron and plasma particle bombardment will put an upper limit to the allowable wall loading. This wall loading is a quantity of prime importance in the design of a fusion reactor.

An additional design parameter of importance is the first wall operational temperature, which, from a thermal efficiency point of view, should be as high as possible.

Both these arguments suggest that the most suitable candidates for the first wall and blanket structural materials in CTR's with optimum economy would be radiation resistant materials having a high melting temperature. Obviously, additional requirements such as mechanical properties in the unirradiated condition, compatibility, neutronics, fabricability and cost will influence the material choice.

A considerable body of experimental data concerning swelling and radiation induced changes of mechanical properties of stainless steels, nickel based alloys and carbon materials exists which emerged from fission reactor programmes. Fission neutron bombardment and, to a smaller extent, ion bombardment and HVEM simulation techniques were used to obtain these data. A clear lack of information exists for the group of the high melting point refractory metals and alloys concerning effects like embrittlement, radiation creep, fatigue, swelling, corrosion and surface damage. Furthermore, although the materials problems that will exist in fusion reactors are similar to many of those encountered in fission reactors, differences in degree as well as some specific new problems do exist. Higher recoil energies, different transmutation and gas injection rates and heavy surface irradiation, all of which may be strongly fluctuating in time, are the main differences with fission reactors. The importance of synergistic effects should be stressed as well.

Clearly much more experimental information and theoretical progress is needed to develop an understanding of the material response to radiation related to operational conditions in CTR's. Because of t limited space for experiments available in existing and planned 14 MeV neutron generators use will have to be made of simulation techniques by means of fission neutrons, ion and electron bombardment to study surface and bulk radiation effects and their effect on mechanical properties. Additional effects, such as compatibility of high temperature materials with coolants need also more detailed investigations. Obviously, the ultimate materials choice, which will have to be a compromise, can be made only following a systematic investigation of the most promising candidate materials. Such a task would require an important increase in the research activity on high-temperature materials and on their behaviour under the complex irradiation environment encountered in CTR's.

* * *

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ACKNOWLEDGMENT. — The authors would like to express their appreciation to their colleagues at J. R. C. and R. C. N., Petten for their comments and suggestions during the preparation of this paper.

Rev. int. Htes Temp. et Réfract., 1976, t. *13*, pp. 250-261

COMMISSION OF THE EUROPEAN COMMUNITY
J. R. C., Ispra Establishment (Italy)

HIGH TEMPERATURE CORROSION IN THE THERMOCHEMICAL HYDROGEN PRODUCTION FROM NUCLEAR HEAT (*)

By

F. COEN-PORISINI and G. IMARISIO

1. *INTRODUCTION*

The objective of the Hydrogen Program is the production of hydrogen by water decomposition, utilizing nuclear heat in a cycle of chemical reactions. The interest in hydrogen production by chemical decomposition of water is based on the possibility of extending the utilization of nuclear energy by using a flexible and clean « energy vector ».

The characteristics of hydrogen are well adapted to a number of industrial applications, and to its use as fuel, considering its « clean » combustion that makes it interesting in the programmes against environmental pollution.

The direct thermal decomposition of water to hydrogen and oxygen in one single step is thermodynamically possible only at about 2,500° C for technically interesting decomposition levels.

When nuclear heat is the only energy source, the process has to be a multistep process, so that it can operate at lower temperatures, well in the range of present day reactors. Water and the intermediate chemical products react in chemical cycles giving hydrogen and oxygen with regeneration of the primary products used which are then recycled.

The activity of the *J. R. C. Ispra* in this field has started with the major goal of investigating the feasibility of chemical cycles for water splitting. A certain number of possible chemical cycles, reported in table I, have been defined within the huge number of potentially useful cycles.

TABLE I. — *Summary table of the chemical cycles.*

No.	Mark	Elements	Max. Temp (°C)	No. of reactions
1	Mark 1	Hg, Ca, Br	780	4
2	Mark 1B	Hg, Ca, Br	780	5
3	Mark 1C	Cu, Ca, Br	900	4
4	Mark 1S	Hg, Sr, Br	800	3
5	Mark 2	Mn, Na (K)	800	3
6	Mark 2C	Mn, Na (K), C	850	4
7	Mark 3	V, Cl, O	800	4
8	Mark 4	Fe, Cl, S	800	4
9	Mark 5	Hg, Ca, Br, C	900	5
10	Mark 6	Cr, Cl, Fe, (V)	800	4
11	Mark 6C	Cr, Cl, Fe, (V), Cu	800	5
12	Mark 7	Fe, Cl	800	5
13	Mark 7A	Fe, Cl	850	5
14	Mark 7B	Mn, Cl	900	3
15	Mark 8	Mn, Cl	900	3
16	Mark 9	Fe, Cl	650	3
17	Mark 10	I, S, N	850	6
18	Mark 11	S (hybrid)	850	2
19	Mark 12	I, S, N, Zn	850	4
20	Mark 13	Br, S (Hybryd)	850	3

These cycles have been differentiated into several « families » and the research is particularly focused on the exploration and evaluation of the different chemical reactions of these « families ».

The chemical cycles listed in the table have been the object of a certain number of investigations: some appear encouraging, others less.

Certain cycles have been defined only very recently, while others have not yet been sufficiently studied

(*) Part of the paper The Compatibility of C[illegible] ab[illegible]ment Materials for Thermochemical Hydrogen Production presented by the authors at the *1st world hydrogen energy c[illegible]nce* (March 1-3, 1976, Miami Beach, USA).

owing to the fact that the total effort of the research is limited and the work had to be concentrated on a few specific reactions. The choice criteria for the various potential cycles are obviously numerous and complicated.

Considerations based only on the chemistry of the reactions are in fact incomplete.

Fundamental information on the problems of materials are essential together with a clear feeling for the various steps involved in the running of a cycle. A preliminary evaluation of such items as: energy needs for concentration, mass movements, separations, etc., are necessary. A net acceptable thermal efficiency is also imperative. Other important parameters to be considered are those related to coupling with a nuclear reactor; the maximum temperature at which nuclear heat is available, the interest in a single or double purpose nuclear reactor, etc.

The study in the field of materials was particularly aimed at defining a list of possible materials for the corrosive environments most frequently present in the thermochemical reactions under study.

Three cycles are mentionad as an example, *i. e.* Mark 1, of the Hg — Br family, Mark 15 of the Fe — Cl family and Mark 16 of the S — I family. The chemical reactions relative to these three cycles are the following:

Mark 1

1)	$CaBr_2+2\,H_2O \rightarrow Ca(OH)_2+HBr$	780º C
2)	$2\,HBr+Hg \rightarrow HgBr_2+H_2$	200º C
3)	$HgBr_2+Ca(OH)_2 \rightarrow CaBr_2+HgO+H_2O$	200º C
4)	$HgO \rightarrow Hg+1/2\,O_2$	600º C

Mark 15

$3\,FeCl_2+4\,H_2O \rightarrow Fe_3O_4+6\,HCl+H_2$	650º C
$Fe_3O_4+8\,HCl \rightarrow FeCl_2+2\,FeCl_3+4\,H_2O$	150-200º C
$2\,FeCl_3 \rightarrow FeCl_2+Cl_2$	300-400º C
$Cl_2+H_2O \rightarrow 2\,HCl+1/2\,O_2$	700º C

Mark 16

$2\,HI \rightarrow H_2+I_2$	600º C
$I_2+SO_2+2\,H_2O \rightleftarrows 2\,HI+H_2SO_4$	R. T.
$H_2SO_4 \rightarrow H_2O+SO_2+1/2\,O_2$	800º C

A characteristic of these reactions is the presence of halide compounds and particularly hydracids at temperatures up to 800º C.

2. CORROSION EXPERIMENTS

Corrosion tests were begun in silica capsules. Each capsule containing one corrosion sample and an appropriate amount of the corrosive agent was sealed under vacuum.

The amount of corrosive agent in each capsule was calculated to provide an internal vapour pressure of not higher than 20 atmospheres at the experimental temperature. Moreover, because of the very small quantity of corrosive used and the high pressure, built up in the capsule during the corrosion tests also from corrosion products, the results obtained were often misleading.

It was therefore decided to carry out some dynamic tests. Small laboratory silica loops were fabricated. Vapour from the corrosive was produced in a boiler, passed into a tube, heated by a furnace and maintained at the desired temperature; a condenser at the outlet of the tube recycled the liquid back to the boiler. The samples suspended inside the tube were maintained in flowing vapour at room pressure.

Figure 1 shows the experimental set-up.

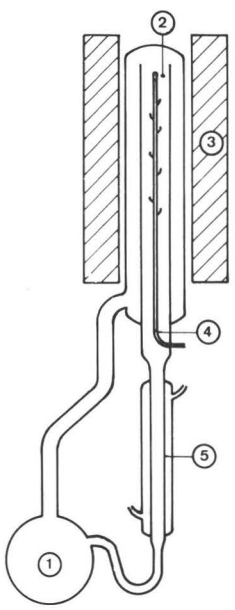

FIG. 1. — *Silica loop for dynamic tests in vapour phase.* (1) *Boiler;* (2) *Reaction tube;* (3) *Furnace;* (4) *Samples holder and temperature control;* (5) *Condenser.*

The post-corrosion examination of the samples included: weight change measurements, optical and scanning electron microscopic examinations, X-ray diffraction analysis of the corrosion products.

3. CORROSIVE ENVIRONMENTS

The corrosive environments examined up to now are:

Hydrobromic, hydrochloric acid, ferric chloride, hydriodic acid.

3.1. Work in Hydrobromic Acid

In order to obtain preliminary orientative information on possible suitable materials for use in hydrobromic acid, it was necessary to carry out screening tests on many materials. Due to the lack of data in the lit ature the choice of materials to be tested was almost un ited.

T rosion tests were carried out in silica capsules at 600º C, 800º C.

R ts are shown in tables II, III, IV.

TABLE II. — *Corrosion tests in hydrobromic acid 48 wt % at 400º C.*

Material	Time, hours	Weight changes mg/cm^2	Remarks
Stainless steel (304 AISI)	500	-44	
Nickel	500	-32	
Hastelloy B	1000	-75	
Hastelloy C	1000	-28	
Nimonic 90	500	-25	
Inconel 625	1000	-25	
Inconel 750	500	-35	
Inconel 600	500	-42	
Incoloy 800	500	-39	
Incoloy 825	1000	-61	
Tantalum	1000	-130	
Molybdenum	2500	+1	
TZM (Mo+0.5 Ti+ 0.1 Zr)	2500	+1	
Mo HT (Mo 99.85+ controlled impurities)	2500	+0.8	
Zircaloy 2	500		Samples were broken
Zr-2.5 Nb	500		
Tungsten	1000	-9	
Zirconia (Zr 23 Degussa)	2000	-5	
Alumina (Al 23 Degussa)	2500	+3	
Alumina (Purox-Morgan)	2500	-0.7	
Alumina (AF 970-997-995 Desmarquest)	2500	-0.2	
Mullite (Desmarquest)	2500	-1.5	
Mullite (Triangle H5 Morgan)	2500	-1.5	
Sillimanite (Type 610 Koppers)	2500	-2.2	

It may be noted that ceramic materials seem to resist the acid attack at these high temperatures quite well.

The metallic materials tested were generally corroded with the exception of molybdenum alloys which showed small weight changes. Microscopic examinations of these samples were not performed because it was decided to carry out dynamic tests. In fact the corrosion phenomenon could change in a dynamic system due to continuous feeding of corroding vapours, lower working pressure and the absence of high pressure from volatile corrosion products.

Dynamic tests were planned to check the results obtained under static conditions but the activities involving bromine compounds were slowed down because of the need to have some information about materials in contact with chlorine compounds.

3.2. **Work in Hydrochloric acid**

Some information on materials in contact with hydrochloric acid at temperatures up to 100-200º C is available from industrial applications in chemical plants. In the case of Fe—Cl cycles, hydrochloric acid is present at temperatures up to 650º C and in some cases at very high concentrations (~80 wt %).

Corrosion tests were carried out in the small silica loops already described.

The selection of metallic materials took into account the results obtained in screening static tests carried out in glass capsules that had shown the good behaviour of Mo—and the promising properties of Ni-based alloys reported in table V. Tests were carried out at 600º C and 700º C. For most of the experiments the hydro-

at 300° C in Cl_2 + HCl (an environment found frequently in the FeCl cycles). Mo, Ta, Zr-alloys TZM have been found to be non-resistant.

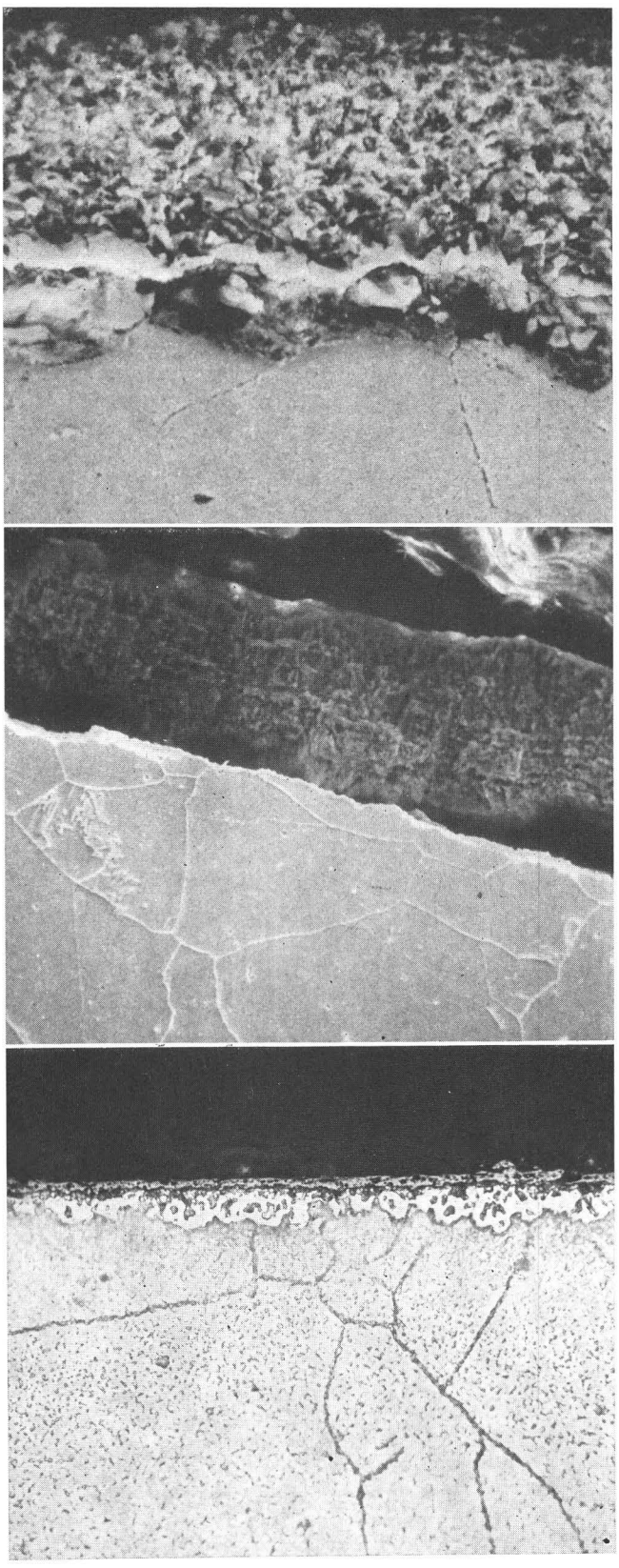

FIG. 6. — *IN 691 S. E. I. of etched cross sections. a)* HCl *21 wt %, 600° C, 1,000 hours* (× 1,000); *b)* HCl *80 wt % 600° C, 1000 hours* (× 300); *c)* HCl *21 wt %, 700° C 500 hours* (× 500).

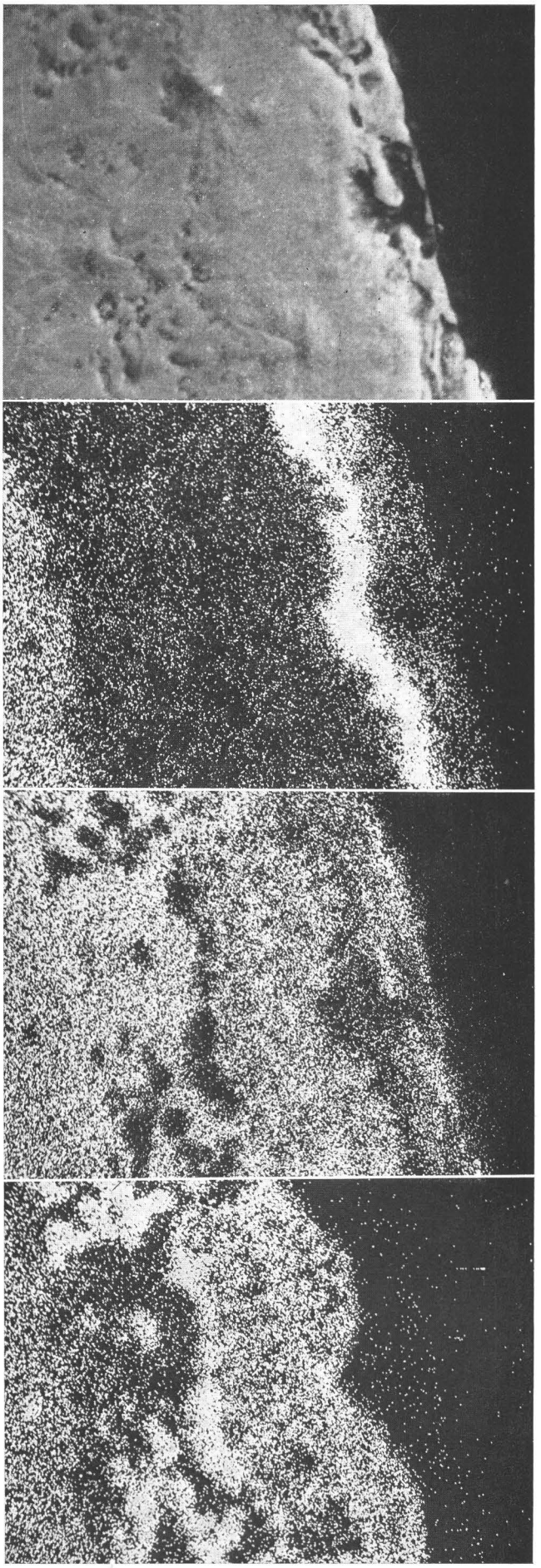

FIG. 7. — *Hastelloy B.* HCl *21 wt %, 600° C, 500 hours. a) S. E. I. of a cross section* (× 1,000); *b)* FeKα-*Xray image showing the diffusion of* Fe; *c)* NiKα-*Xray image showing the redistribution of* Ni; *d)* MoLα-*Xray image showing the distribution of* Mo.

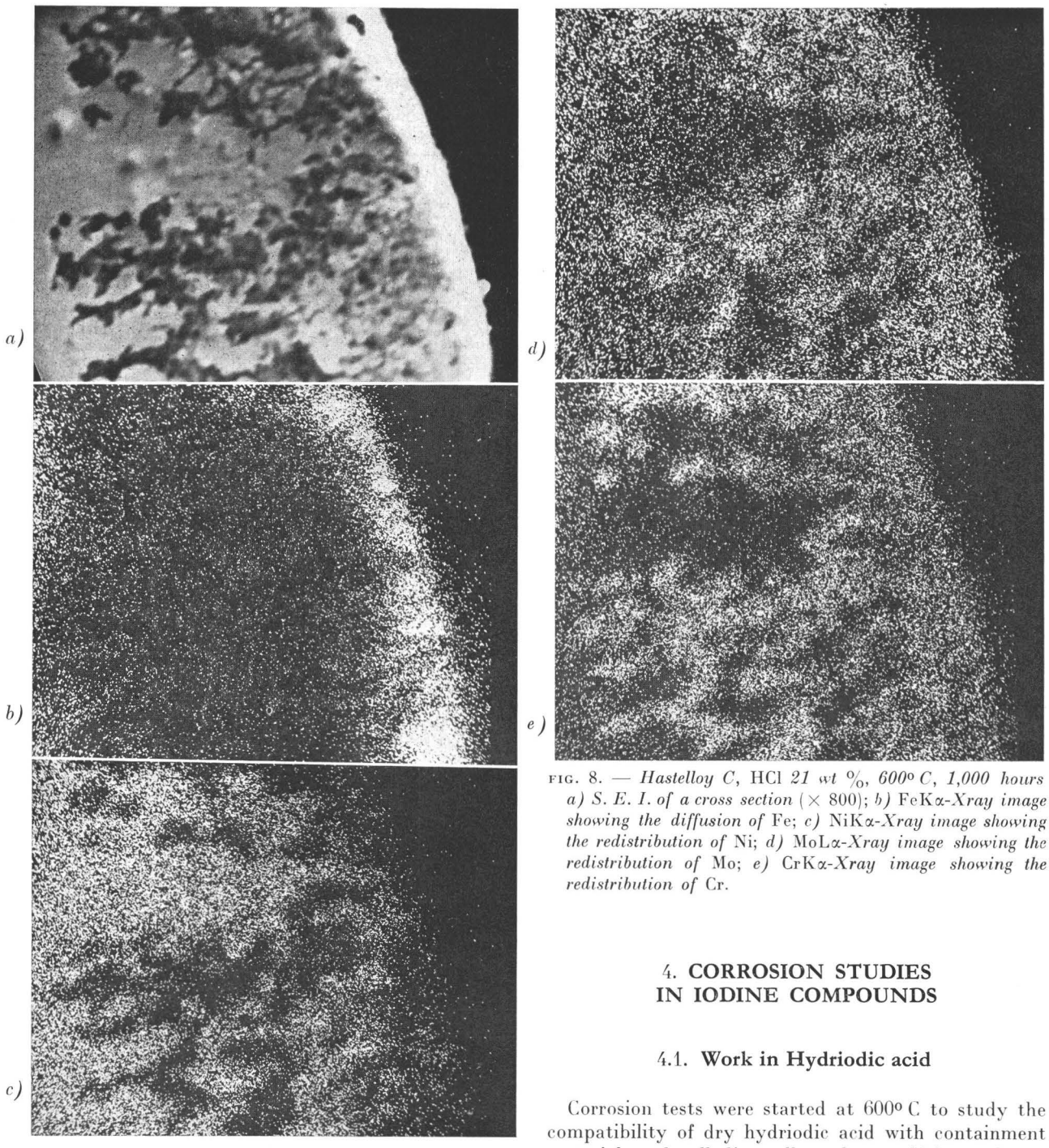

FIG. 8. — *Hastelloy C*, HCl *21 wt %, 600° C, 1,000 hours a) S. E. I. of a cross section* (× 800); *b)* FeKα-*Xray image showing the diffusion of* Fe; *c)* NiKα-*Xray image showing the redistribution of* Ni; *d)* MoLα-*Xray image showing the redistribution of* Mo; *e)* CrKα-*Xray image showing the redistribution of* Cr.

FIG. 8.

4. CORROSION STUDIES IN IODINE COMPOUNDS

4.1. Work in Hydriodic acid

Corrosion tests were started at 600° C to study the compatibility of dry hydriodic acid with containment materials and palladium alloys that could be used as a

TABLE IX. — *Corrosion tests in hydrochloric acid solutions at 700° C (tests in silicaglass loops).*

Material	Δp mg/cm²	
	HCl 21 wt% 4240 h	HCl 80 wt% 3000 h
Alumina (Al 23-Degussa)	+0.1	0
Alumina (Purox-Morgan)	+0.5	+0.2
Alumina (AF 970-Desmarquest)	-0.1	+1
Mullite (Desmarquest)	-0.2	0
Mullite (Triangle H5-Morgan)	-0.2	+1.5
Sillimanite (Type 610-Koppers)	-0.6	-0.3
Triangle H (Morgan)(Aluminous porcelain)	-0.4	+0.4
Zirconia (Zr 23-Degussa)	+1.3	-20

TABLE X. — *Corrosion in* $FeCl_3$ *(vapour phase) (weight changes in mg/cm²).*

A) at 150° C

Material \ Time, h	720	1,440	2,160	2,880	5,040
Teflon. . .	— 0.06	— 0.02	—	0	0
Tantalum .	+ 0.07	+ 0.07	—	0	+ 0.11
Molybdenum.	— 4.19	—	— 12.19	—	— 23.65

Non-resistant materials: AISI 430, AISI 440, Zr-2.5-Nb, Zr-1Cu-0.4Fe, Zr-0.8Fe-0.8V, Zircaloy-2, Monel 400, Hastelloy C, Incoloy 825, Nickel 201, Inconel 625, Ti 0.2 Pd.
Previously oxidized stainless steels and zirconium alloys did no better.

B) at 420° C

Material \ Time, h	720	2.160	3,600
Sillimanite . .	— 0.06	— 0.43	— 0.45
Vitreous Carbon.	— 2.4	—	—
Silicon nitride .	—	+ 18.07	+ 18.90
Silicon carbide .	—	— 0.78	— 0.57

Non-resistant materials (in addition to those reported above): Mo, Ta, TiB, TiC.

TABLE XI. — *Corrosion in* Cl_2 *96 %* HCl *4 % at 300° C weight changes in mg/cm².*

Material \ Time, h	720	2,160	3,600
Mullite . . .	— 0.08	— 0.08	— 0.08
Vitreous Carbon.	— 1.45	— 0.54	+ 0.86

permeable window for the continuous separation of H_2 produced by thermal decomposition of HI. A laboratory silica loop with an all glass magnetic pump to circulate the HI has been designed and constructed (fig. 9).

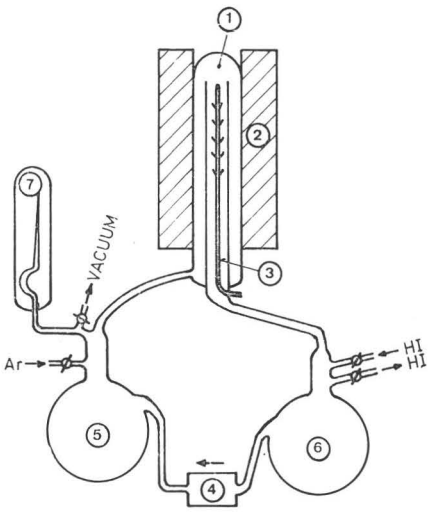

FIG. 9. — *Silica loop for dynamic tests in dry HI.* (1) *Reaction tube;* (2) *Furnace;* (3) *Samples holder and temperature control;* (4) *Glass magnetic pump;* (5, 6) *Reservoir;* (7) *Glass manomer.*

The alloy Pd-25 % Ag is, as was expected, considerably corroded. New Pd alloys, prepared at the J. R. C.-Ispra seem to behave satisfactorily.

CONCLUSIONS

The work presented here is relative only to the preliminary screening of materials of possible utility in the cycles actually under development.

This kind of exploratory work will be continued until eventually a definitive cycle will be chosen as the most promising. The work on corrosion and choice of suitable materials will then become one of the most important points in the cycle development and then all the specific problems connected with the chosen cycle will require a complete study to reach acceptable solutions also from a plant engineering point of view.

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DISCUSSION

SECTION 3

P. Kofstad. — Mrs. Anthony, you considered various oxides as insulating material. One group of oxides with high stability and low electrical conductivity are the rare earth oxides, yttrium oxide for example. How would that fit in this connection?

A.-M. Anthony. — I think rare earth oxides are quite problematic for this purpose. At those temperatures they become electrical conductors better than magnesia.

C. Edeleanu. — I have a question and two comments on Mrs. Coen's and Mr. Imarisio's paper.

What sort of order of thermal efficiency is one obtaining from these cycles?

I would advise you to look up the literature on the old bismuth cooled reactor which was countercooled with molten chlorides. You will see that in that work the thermodynamics and the phenomena that you are talking about have been reasonably well studied up to 800° C. I am sure you will find that glass is part of your electrolyte at the temperatures you are working at. You will almost certainly have found that glass embrittles and a lot of the corrosion phenomena you are observing are as much associated with the nature of the glass as the nature of the chemicals you are using. The chemicals are only a means of transporting ions from glass on to the metal and the other way around.

F. Coen-Porisini. — We know this, we found in the liquid silicon oxide.

G. Imarisio. — The question of thermal efficiency is depending on the kind of cycle under study. Due to the fact that no cycle has been chosen for the final exploitation and to the fact that all the work in the hydrogen programme is in the first stage of small scale tests, all the calculations have been done on the basis of very preliminary data. This calculation used the data produced by the hydrogen programme, and where this data was insufficient, made reasonable assumptions from literature data. The general outcome showed an efficiency of up to 40-42 %, taking into account losses from the heat exchangers and in the heat exchangers.

Of course this is a very rough estimation because of the very rough starting point. Also a sensitivity analysis has been made using computers to find out what the parameters were to which the system was sensitive and to find out what was the assumable error of the estimation. In general you can think of an error of about 5 % in the estimation of the efficiency. Much better computations could be done when more data is accumulated during the work in this programme.

C. Edeleanu. — I would like to ask a question to Mrs. Anthony. I wonder whether any studies have been carried out on the conductivity of hydrocarbon gases which have free radicals in them. I have a suspicion that one would get reasonable conductivities at far lower temperatures than the temperature at which you have been working. Since such gases exist in the industry and have to be cooled, what better method of cooling them than by making electricity out of them by your method?

A.-M. Anthony. — I think the problem is the magnetic field. The conductivity of the gas is one problem, to get a good magnetic field for this is another problem. If we can improve the magnetic field, I think it is o. k., but I think even with free radicals it is too low.

H. Walther. — I would like to ask Dr. Bressers a question on the subject of hydrogen embrittlement in high-temperature materials. It is clear that hydrogen can diffuse in, but heating the materials is also used to overcome the hydrogen embrittlement problem making the hydrogen diffusing out. Is there really evidence that hydrogen embrittlement occurs at the high temperature?

J. Bressers. — Hydrogen isotopes can become effectively trapped in metals at higher temperatures by radiation induced point defects. This changes the diffusion characteristics controlling outgassing of hydrogen. Experimental information concerning this effect is almost non existing, so one cannot exclude *a priori* the possibility of hydrogen embrittlement.

H. Nickel. — Mrs. Anthony, I am wondering why graphite is not considered as material for MHD converters. With graphite we have an excellent material from the point of view of temperature stability and also

radiation effects. You have no radiation effects in this case, but is it in your case a question of cesium, that you have corrosion, or what is the reason that you have listed graphite but given no clear answer on its use? My feeling is that graphite is a very good material for such requirements.

A.-M. ANTHONY. — The first MHD tests in open cycle were made with graphite, but, unfortunately, the oxygen potential was too high.

H. NICKEL. — My question refers to the closed cycle.

A.-M. ANTHONY. — For a closed cycle one can also use metals but in the open cycle it is impossible.

H. NICKEL. — May I question Dr. Bressers on the subject of graphite? You mentioned how many ppm helium per year are collected in the different materials. Can you explain why this is in graphite and in silicon carbide so extremely high compared with the metals?

Another question: Why have you not given results of pyro-carbon, for example, isotropic pyro-carbon or silicon carbide as wall material?

J. BRESSERS. — Silicon carbide as well as graphite are considered as possible candidate materials for the first wall of fusion reactors. The high helium concentrations generated in these materials by transmutation reactions upon 14 MeV neutron bombardment are due to the high reaction cross-sections and the nuclear transmutation reaction involved ($C(n, n')3\alpha$).

V. COEN. — In replying also to Prof. Nickel's question, I think you have to take into consideration the effect of the 14 MeV neutrons, and this is practically the main difference for the materials in a fission reactor with respect to a fusion reactor; there is no experience at all on the irradiation properties. Only now the U. S. A. are beginning to install installations to make irradiations with 14 MeV neutrons. Graphite is, of course, taken into consideration as a low zeta material, but I mean you must also take into consideration the amount of hydrogen and hydrogen isotope present in a CTR reactor, and this will certainly be a problem.

I would like to add something to the hydrogen embrittlement question that Dr. Walther raised. From my point of view the problem is not a high-temperature embrittlement; it is more related to the reactor operation. You have shut downs and you go down with temperature, and at that moment you form stable hybrides. If you do not have a coating on your material or if you do not use a material that is resistant to hydrogen at high and low temperatures, well then you have a problem.

J. BRESSERS. — I agree with Dr. Coen that hybride formation upon lowering the temperature results in embrittlement problems. But I would like to stress again that the possibility of hydrogen embrittlement at higher temperatures cannot be excluded *a priori*.

M. VAN DE VOORDE. — One short word about hydrogen embrittlement enhanced by radiation. I know that recently a National Committee on Radiation Damage was set up in the U. S. A. They are looking into the effects of 14 MeV radiation and in particular its effect on hydrogen embrittlement at high temperatures. Although a 14 MeV machine is very expensive, it would be a very useful installation to have in Europe. The only thing that can be done at present, is to simulate this radiation field by using a reactor source. I think the data presented by Bressers and van Witzenburg has made this clear.

I would like to ask Mrs. Anthony a question. What is the relation between the fabrication of ceramic materials and their end properties?

A.-M. ANTHONY. — I think it is the main problem of ceramics. If we can improve the fabrication of ceramics, we can improve the properties. I can give an example. Ten years ago we used only brick fire clay for insulating. If you are operating a furnace at 2,000° C, the brick breaks completely. Now there is a new structure of ceramics. In our laboratory we now use a lot of fiber in ceramics, we can put it in 2,000° C in air, and we have no failures after many hours. I think if we work more on the structure of ceramics, we can improve greatly the weakness of ceramics and the mechanical properties.

M. VAN DE VOORDE. — What about the reliability, the statistical errors, reproducibility in fabrication and so on?

A.-M. ANTHONY. — Usually ceramics are not as reproducible as metals. Before MHD work had begun, *e. g.* the experimental results for the electrical conductivity of alumina differed by 5 or 6 orders of magnitudes. With MHD tests we improved to 10 % error, and today we can make experiments at better than 1 %.

FIRST PETTEN COLLOQUIUM
ON
ADVANCED HIGH TEMPERATURE MATERIALS:
TECHNOLOGICAL AND INDUSTRIAL ASPECTS (*)

SECTION 4

MATERIALS

(*) The *Section 1* of proceedings of that *Colloquium*, organized by the *Commission of the European Communities*, on January 29 and 30, 1976 in Petten (the Netherlands), as be published in the *Revue Internationale des Hautes Températures et des Réfractaires*, 1976, *13*, nº 3, pp. 139-185 and *Sections 2* and *3* in 1976, *13*, nº 4, pp. 189-263.

Rev. int. Htes Temp. et Réfract., 1977, t. *14*, pp. 6-20

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HIGH TEMPERATURE OXIDATION AND CORROSION OF METALS AND ALLOYS

By

J. STRINGER and D. P. WHITTLE

1. *INTRODUCTION*

In its most general sense, the high temperature oxidation of a metal means its reaction with constituents of its gaseous environment: these can include not only oxygen, but also nitrogen, sulphur, carbon, chlorine, etc. In practical situations one is usually concerned with the resultant degradation of those properties of the metal or alloy which determined its use in the first place: most commonly these are mechanical properties. This degradation is often associated with the formation of a discrete reaction product: an oxide (nitride, sulphide, etc.), or with the removal of metal. Thus, since the mechanical strength of an oxide layer in tension is normally negligible, the oxidation has the effect of reducing the load-bearing cross-section of the metallic component as metal is consumed. The effect on the mechanical properties may greatly exceed the apparent overall reduction in section, however: thus the oxide may not form uniformly on the metal surface, but may penetrate locally to much greater depths, for example at grain boundaries: the effect of this is to reduce the cohesion of the metal. The degradation, however, may not be associated with the formation of a discrete oxide product or the removal of metal: thus, titanium dissolves oxygen and nitrogen at elevated temperatures embrittling the metal.

Sometimes the problem is associated with the reaction product itself, and not with the degradation of the metal: thus, mild steel bolt assemblies in the Magnox reactors suffered an accelerated oxidation in CO_2, the magnetite (Fe_3O_4) layers on the washers forcing the assemblies apart, applying a very large tensile stress to the bolts. In boilers, oxide may form in the reheater tubes on the steam side and exfoliate; the fragments are then carried into the turbine and can cause erosion of the blading. Heat transfer properties of surfaces are also affected when scaling takes place.

The presence of more than one oxidant can cause special problems. For example, many high temperature alloys depend on the formation of an external chromia (Cr_2O_3) protective scale; however, if the alloy is carburised first, the chromium is removed as a chromium-rich carbide, $M_{23}C_6$, and on subsequent oxidation it appears difficult to form a protective oxide. There are many other examples, and this problem will be examined in more detail later.

The term « corrosion » usually implies the presence of a liquid medium and a predominantly electrochemical mechanism of reaction; but, in high temperature technology the term has come to be somewhat more loosely applied. « Hot corrosion » is a specific process which certainly appears to involve the presence of a liquid salt layer, but it is to say the least, debatable whether it acts as an electrolyte in a process analogous to that in low temperature corrosion.

In this review, the thermochemistry of the oxidation process will be summarised first. The mechanism of oxidation of alloys will then be described, first in environments involving a single oxidant and then in environments involving two or more oxidants. Finally, the processes that can take place in the presence of a molten salt species will be reviewed. It is clearly impossible to give a comprehensive review in this limited space, but some of the more important practical problems will be mentioned.

2. THERMODYNAMICS OF OXIDATION

2.1. Pure Metal and a Single Oxidant

The simplest situation is a pure metal reacting with a single oxidant to form a single, solid oxide: if the oxidant is in the gas phase as a simple molecule, for

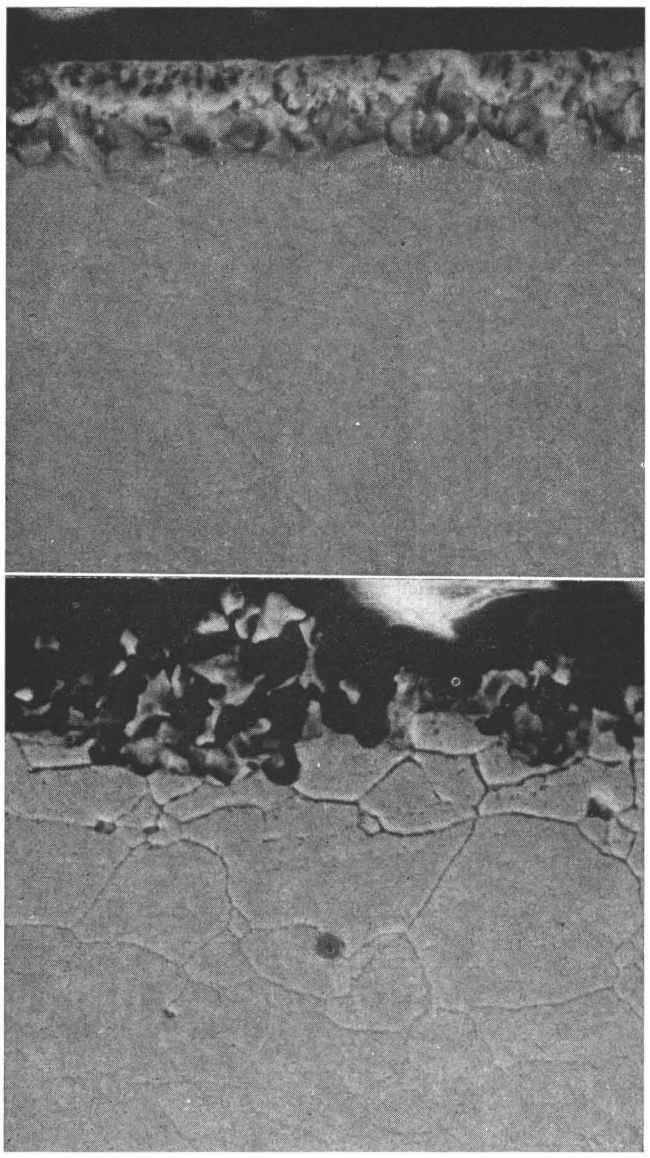

FIG. 4. — *Inconel 600. S. E. I. of etched cross sections. a)* HCl *21 wt %, 600º C, 1,000 hours* (× 1,000); *b)* HCl *80 wt %, 600º C, 1,000 hours* (× 1,000).

— The corrosion products determined by X-ray diffraction analysis on a certain number of alloys, show mainly the presence of oxides. In many cases the presence of partly crystallised compounds is evident. The formation of chlorides should not be excluded since these compounds are volatile at the test temperatures.

— The S. E. M. X-ray images of the alloy components have shown a mobility of Fe not only in the corrosion layers but sometimes also in the bulk of the alloy.

Fe depletion is evident in the bulk of Hastelloy B, together with a redistribution of Mo and Ni (fig. 7).

This phenomenon is limited to the corrosion layer in the case of Hastelloyc C (fig. 8) and other alloys.

Ceramic materials were also tested in the silica loops and the results obtained are reported in table IX.

3.3. **Work in Ferric Chloride Solutions**

Corrosion tests were carried out in glass capsules. Table X shows the corrosion behaviour of different

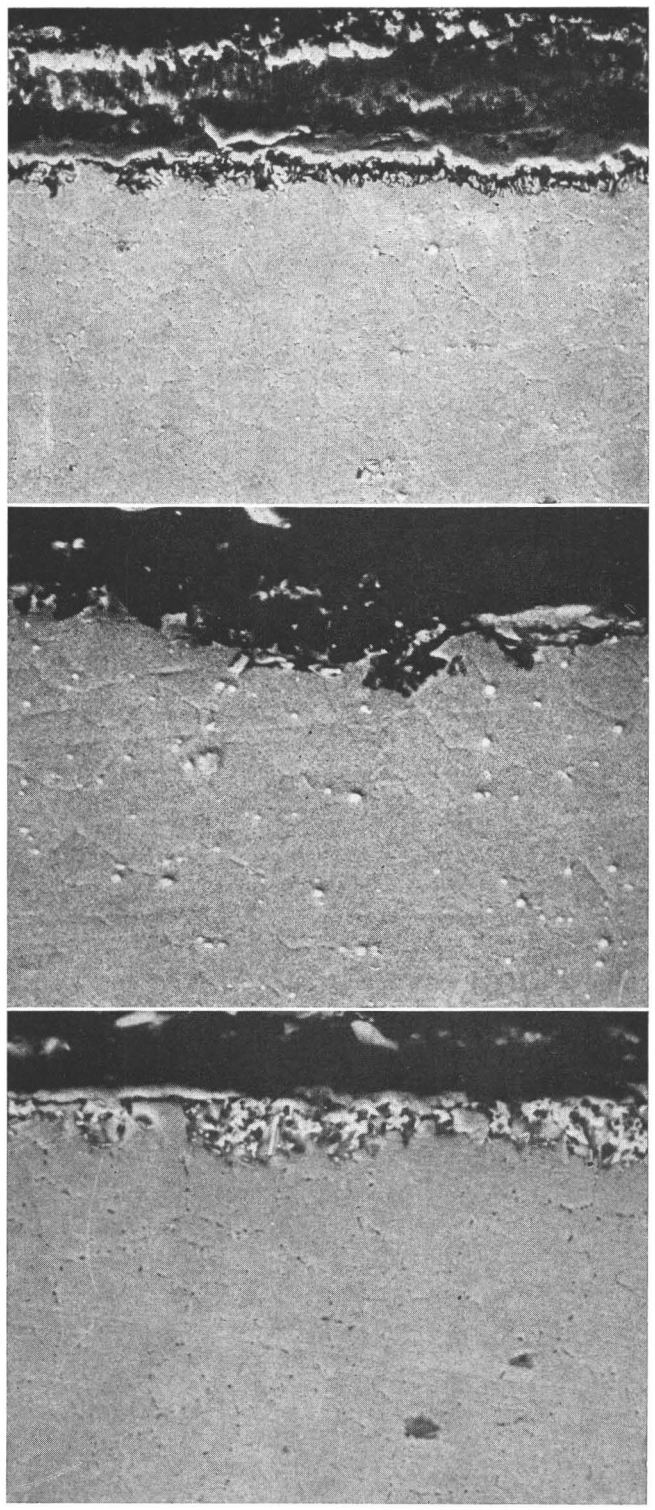

FIG 5. — *Inconel 625 S. E. I. of etched cross sections. a)* HCl *21 wt %, 600º C, 1,000 hours* (× 500); *b)* HCl *80 wt %, 600º C, 1,000 hours* (× 1,000); *c)* HCl *21 wt % 700º C, 500 hours* (× 1,000).

materials in $FeCl_3$ at two temperatures. This environment is one of the most severe so far examined. Only these few reported materials show a reasonable behaviour.

For each temperature the table also reports discarded materials. Table XI shows the corrosion of Mullite

— The post-corrosion examination of samples which had been subjected to tests for up to 500 hours, led to the rejection of materials showing deep internal corrosion or intergranular corrosion.

— For promising materials, longer exposure times were envisaged.

A maximum of 2,000 hours has been reached up to now.

The importance of carrying out long-term corrosion tests resides in the fact that the actual form taken by the corrosion is not frequently evident from short duration tests.

In the case of alloy 6X (fig. 2) the intergranular corrosion in the 21 % solution appeared after 1,600 hours, while nothing was seen after 1,000 hours.

— Materials such as Hastelloy C and Inconel 600, showed a slow and uniform corrosion in the 21 % solution, but intergranular corrosion in the more concentrated solution (fig. 3, 4).

— Of all the metallic materials tested up to now, Inconel 625, and IN 691 seem to be most promising for the experimental conditions envisaged (fig. 5, 6). Both materials show uniform corrosion, but long duration tests are necessary to confirm these results.

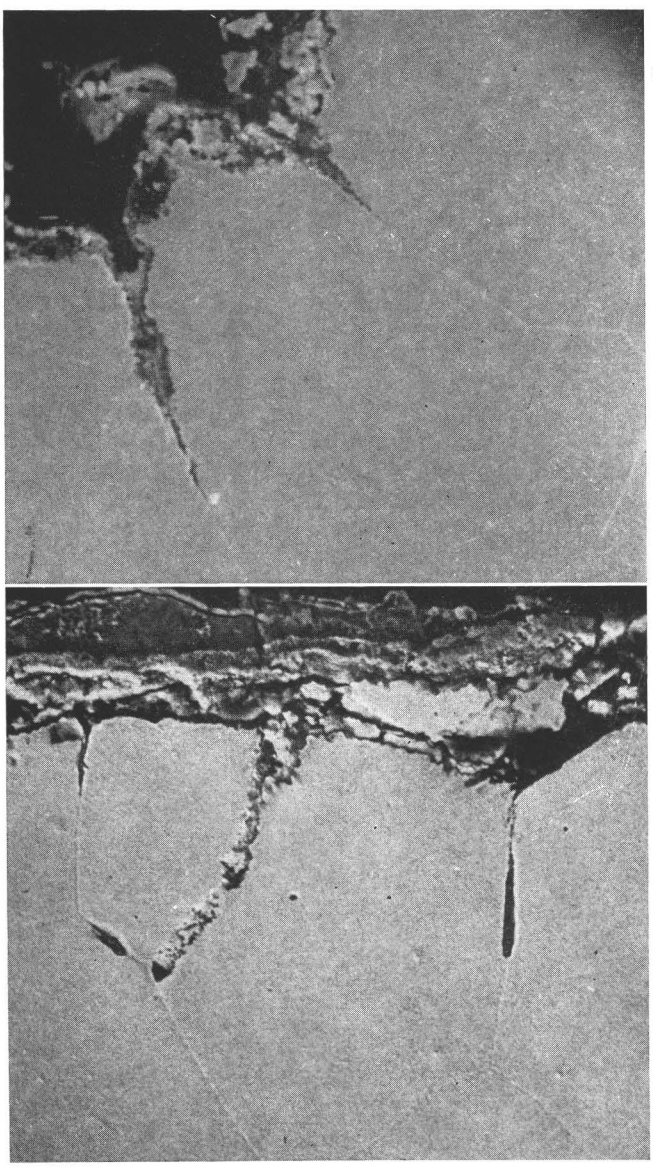

FIG. 2. — *6X S. E. I. of etched cross sections. a)* HCl *21 wt %, 600º C, 1,670 hours* (× 500); *b)* HCl *80 wt %, 600º C, 500 hours* (× 500).

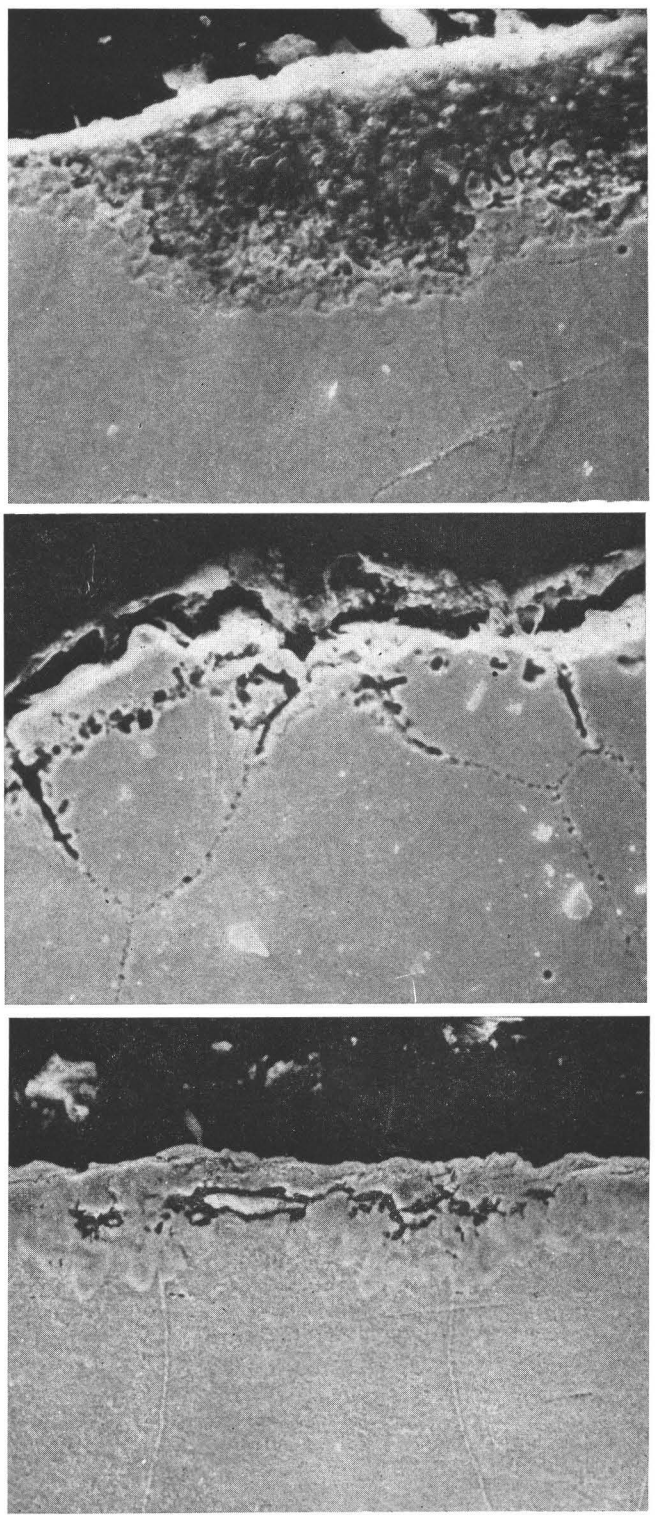

FIG. 3. — *Hastelloy C, S. E. I. of etched cross sections. a)* HCl *21 wt %, 600º C, 2,000 hours* (× 1,000); *b)* HCl *80 wt %, 600º C, 500 hours* (× 1,000); *c)* HCl *21 wt %, 700º C, 500 hours* (× 1,000).

TABLE VI. — *Corrosion tests in hydrochloric acid solution 21 wt % at 600° C (tests in loops).*

Material	Time in hours	Δp mg/cm²	Thickness of corrosion layer (Remarks from microscopic examination)	Corrosion products by X-ray diff. an. in decreasing order of peak magnitude
Molybdenum	1000	-2.2	non adherent corrosion layer of approx. 15 μ thickness	MoO_2
TZM (Mo+0.5Ti+0.1Zr)	1000	-2.3	non adherent corrosion layer of approx. 15 μ thickness	
Hastelloy B	500	-3	~ 70 μ diffusion of Fe towards the surface	$NiO + MoO_2 + Ni + NiFe_2O_4$
Hastelloy C	500 1000 2000	0 0 +0.3	no corrosion ≤ 40 μ. The penetration of 40 μ has been observed in only one isolated zone. Diffusion of Fe towards the surface ~ 40 μ (observed in extended zones)	$MoNi_4 + NiO + MoO_2 + Cr_2O_3$
Inconel 600	500 1000	+0.3 +5.3	~ 10 μ. Weak diffusion of Cr towards the surface ~15 μ.	$Ni + Cr_2O_3$
Inconel 625	500 1000	-0.6 -12.3	~ 20 μ. No diffusion of the components shown ~40 μ	$Fe_2O_3 + NiFe_2O_4 + Cr_2O_3 + MoO_2 + NiCl_2$
Incoloy 825	500	-3	~ 25 μ. Diffusion of Fe towards the surface. Voids formation along grain boundaries	
Incoloy 800	500	-0.1	~ 30 μ. No diffusion of the components shown.	
Ni 200	500	-7.3	~ 80 μ. Intergranular attack	
Ni 201	500	-5	~ 70 μ. Intergranular attack	
Permanickel 300	500	-2.7	~ 20 μ. Intergranular attack	
IN 691	500 1000	-0.1 +2	~ 20 μ. The corrosion layer is lacking in Fe and Ni, while Cr and Mo are present ~ 45 μ	$Cr_2O_3 + \alpha Fe_2O_3 + MoNi_3$
IN 793	500	-1.8	~ 20 μ. Intergranular attack Weak diffusion of Cr towards the surface	
IN 549	500	-1.8	~ 20 μ. Intergranular attack Weak diffusion of Cr towards the surface	
6 X	500 1000 1670	-0.2 +0.6 -2	~ 1 μ. Very thin non-adherent corrosion layer in which Fe and Ni are lacking, while Cr and Mo are present ~ 15 μ ~ 100 μ. Intergran[illegible]tack	[illegible] $Ni + Cr_2O_3$

TABLE VII. — *Corrosion tests in hydrochloric acid solution 80 wt % at 600º C (tests in loops).*

Material	Time in hours	Δ p mg/cm^2	Thickness of corrosion layer (Remarks from microscopic examination)	Corrosion products by X-ray diff. an. in decreasing order of peak magnitude
Hastelloy B	500	-14.5	~ 20 µ	$Ni + MoNi_4 + MoO_2$
Hastelloy C	500	-12	~ 20 µ. Intergranular attack. Cr and Mo diffuse toward the surface	$MoNi_4 + Ni + MoO_2 + Cr_2O_3$
Inconel 600	500 1000	-13.5 -40	~ 25 µ. ~ 20 µ. Intergranular attack.	$Ni + Cr_2O_3$
Inconel 625	500 1000	-5.6 -45	~ 40 µ ~ 5 µ	$Fe_2O_3 + Cr_2O_3 + MoO_2$
Incoloy 800	500	-44	~ 100 µ.	
Incoloy 825	500	-12	~ 10 µ. Intergranular attack	
IN 691	500 1000	-14.5 -49	~ 50 µ ~ 80 µ	$\alpha Fe_2O_3 + NiCl_2.4H_2O + Fe_3O_4 + FeCl_2.4H_2O$
IN 793	500	-19	~ 60 µ Intergranular attack	
I N 549	500	-26	~ 100 µ Intergranular attack	
6 X	500	-41	~ 150 µ. Intergranular attack Mo, Ni and Cl are present in the cracks while Fe and Cr are absent. Cr, Ni and Mo are present in the outside of the corrosion layer	$Ni + Cr_2O_3$
Mo	1000	-144		
TZM	1000	-73		

TABLE VIII. — *Corrosion tests in hydrochloric acid solution 21 wt % at 700º C (tests in loops).*

Material	Time in hours	Δ p mg/cm^2	Thickness of corrosion layer (Remarks from microscopic examination)	Corrosion products by X-ray diff. an. in decreasing order of peak magnitude
Hastelloy B	500	-7.5	~ 100 µ	$NiO + MoO_2 + Ni + NiFe_2O_4$
Hastelloy C	500	-0.3	~ 15 µ. Diffusion of Fe and Cr towards the surface. Mo and Ni are present in the corrosion layer	
Inconel 625	500	-0.1	~ 10 µ. Diffusion of Cr towards the surface. Ni, Fe and Mo are present in the inside of the corrosion layer	$Fe_2O_3 + NiFe_2O_4 + NiO + MoO_2 + Cr_2O_3$
Incoloy 825	500	-1	~ 30 µ. Voids formation along grain boundaries	
IN 691	500	-2.1	~ 20 µ. Diffusion of Cr towards the surface. Fe and Ni are present in the surface. Mo is present in the whole corrosion	$Fe_2O_3 + NiFe_2O_4 + Cr_2O_3 + MoO_2 + NiO$

TABLE IV. — *Corrosion tests in hydrobromic acid 48 wt % at 800° C.*

Material	Time, hours	Weight changes mg/cm^2	Remarks
Nickel	500	-25	Surface heavily attacked
Hastelloy B	500	+5	Surface covered with thick nonadherent corrosion layers
Hastelloy C	500	-1	
Inconel 625	500	-10	The surface of samples was covered with thick nonadherent corrosion layers. Probable pits underneath
Inconel 750	500	-14	
Inconel 600	500	-23	
Incoloy 800	500	+8	
Incoloy 825	500	-15	
Tantalum	170		Samples were broken
Tungsten	170		Samples were broken
Molybdenum	1500	-4	
TZM (Mo+0.5 Ti+0.1 Zr)	1500	-0.8	Thin dark coating on the surface
Mo^{HT} (Mo 99.85 + controlled impurities)	1500	-6	
Gold	500	0	
Alumina (Al 23 Degussa)	2000	+2	
Alumina (Purox-Morgan)	2000	+3.5	
Alumina (AF 970-Desmarquest)	2000	-60	
Mullite (Desmarquest)	2000	+5	
Mullite (Triangle H5 Morgan)	2000	+6	
Sillimanite (Type 610 Koppers)	2000	+4.5	

TABLE V. — *Composition of Ni-alloys tested.*

Alloy	Composition wt%
Hastelloy B	Ni 61, Co 2.5, Cr 1, Mo 28, Fe 5, C 0.05, others 3
Hastelloy C	Ni 54, Co 2.5, Cr 15.5, Mo 16, W 4, Fe 5.5, C 0.08, others 3
Inconel 600	Ni(+Co) 72, Fe 6-10, Cr 14-17, Cu 0.5, Mn 1, C 0.15, Si 0.5, S 0.015
Inconel 625	Ni bal, Cr 20-23, Mo 8-10, Co 1, Fe 5, Al 0.4, Ti 0.4, Nb+Ta 3-4, C 0.1, Mn 0.5, Si 0.015, P 0.015
Incoloy 800	Fe bal, Ni 30-35, Cr 19-23, Al 0.15-0.6, Ti 0.15-0.6, Cu 0.75, Si 1, Mn 1.5, C 0.10, S 0.015
Incoloy 825	Fe bal, Ni 38-46, Cr 19.5-23.5, Mo 2.5-3.5, Al 0.2 max, C 0.05 max, Mn 1 max, Ti 0.6-1.2, Cu 1.5-3, Si 0.5 max, S 0.03 max
Ni 200	Ni(+Co) 99.0 min, C 0.15 max, Mn 0.35 max, Fe 0.4 max, S 0.01 max, S 0.35 max, Cu 0.25 max
Ni 201	Ni(+Co) 99.0 min, C 0.02 max, Mn 0.35 max, Fe 0.4 max, S 0.01 max, Si 0.35 max, Cu 0.25 max
Permanickel 300	Ni(+Co) 97.0 min, C 0.4 max, Mn 0.5 max, Fe 0.6 max, S 0.01 max, Si 0.35 max, Cu 0.25 max, Ti 0.2-0.6, Mg 0.2-0.6
IN 691 (*)	Fe bal, Ni 35, Cr 17.5, Mo 9, Cu 1.5
IN 793 (*)	Fe bal, Ni 34, Cr 20, Al 1.8
IN 549 (*)	Fe bal, Ni 43, Cr 21, Al 2.5
6 X (*)	Fe bal, Ni 23.6, Cr 20.4, Mo 6.5, C 0.038, P 0.013, Mn 1.7, Si 0.81, S 0.004

(*) Samples supplied by courtesy of International Nickel.

TABLE III. — *Corrosion tests in hydrobromic acid 48 wt % at 600° C.*

Material	Time, hours	Weight changes mg/cm^2	Remarks
Stainless steel (AISI 304)	500	-120	Scaling on the surface
Nickel 200	1500	-77	Surface heavily attacked
Nickel 201	500	-21	
Hastelloy B	1500	-63	
Hastelloy C	500	-53	
Nimonic 90	500		Samples were cracked
Inconel 625	500	-12	The surface of samples was covered with thick non aderent corrosion layers. Probable pits underneath.
Inconel 750	500	-22	
Inconel 600	500	-24	
Incoloy 800	500		Samples were broken
Incoloy 825	500		Samples were broken
Tantalum	336	-160	
Tungsten	336	-38	
Rhenium	336	-4	
Iridium	336	0	
Zircaloy 2	336		Samples were hydrided (4000 ppm H_2)
Zr-2.5 Nb	336		Samples were hydrided (400 ppm H_2)
Molybdenum	1500	-2.5	
TZM (Mo+0.5 Ti+0.1 Zr)	2000	-8	Thin coating on the surface
Mo HT (Mo 99.85 + controlled impurities	2000	+2.5	
Zirconia (Zr 23 Degussa)	2000	-4	
Alumina (Al 23 Degussa)	3000	+0.7	
Alumina (Purox-Morgan)	3000	+0.5	
Alumina (AF 970-997-Desmarquest)	3000	+0.8	
Mullite (Desmarquest)	3000	-0.3	
Mullite (Triangle H5 Morgan)	3000	-0.3	
Sillimanite (Type 610 Koppers)	3000	-0.3	

chloric acid used was a solution of 21 wt %. Some tests have been done with hydrochloric acid of 80 wt % (in the vapour phase).

The post-corrosion examination of the samples includes weight change measurements, without removal of corrosion products, and microscopic examinations.

Many materials tested showed internal corrosion (intergranular corrosion, changes in the microstructure and/or void formation) and for this reason weight changes alone were not sufficiently indicative to evaluate the corrosion resistance. The samples were monted in resin and the cross sections were metallographically polished with diamond paste.

All efforts were made to keep the corrosion layers intact so that the composition of those layers could be investigated and the role of the single components of the alloy in the corrosion phenomenon could be assessed.

The samples were examined under optical or scanning electron microscopes. In an attempt to obtain some understanding of the corrosion mechanism, X-ray images were taken of each single component of the alloy in order to detect any change in composition due to the corrosion phenomena. The presence of Cl in the corrosion zone was also investigated.

Redistribution of some of the elements and internal diffusion were evidenced in many alloys. The samples were then metallographically etched to show grain structure and intergranular corrosion, if any. The thickness of the corrosion layer (including internal attack) was measured.

X-ray diffraction analysis of the corrosion layers was carried out directly on the samples in order to identify the corrosion products. Tables VI, VII, VIII report the results obtained so far. From the information in the tables the following comments can be made:

example O_2, then because the activities of the metal and the oxide may be taken as unity, the dissociation pressure of the oxide may be simply related to its standard free energy of formation.

If the oxidant is not present as a single molecular species the calculation becomes a little more involved, since several reactions must be considered, together with the reactions representing the equilibria between the different polymers of the gas phase; however, in the majority of practical situations, this is not a problem.

It is common to plot standard free energies of formation as a function of temperature for the pure metals; then since the ordinate is also related to the dissociation pressure, pressures above the line would result in oxidation, the oxide phase being stable; pressures below the line correspond to regimes where the metal phase is stable. This diagram is called an Ellingham diagram, and examples can be found in the literature [1] of diagrams for most of the common components of high temperature alloys for reactions with oxygen; analogous diagrams are available for reactions with other single oxidants, sulphur, nitrogen, etc. Figure 1 shows a simplified version containing lines for a number of common elements.

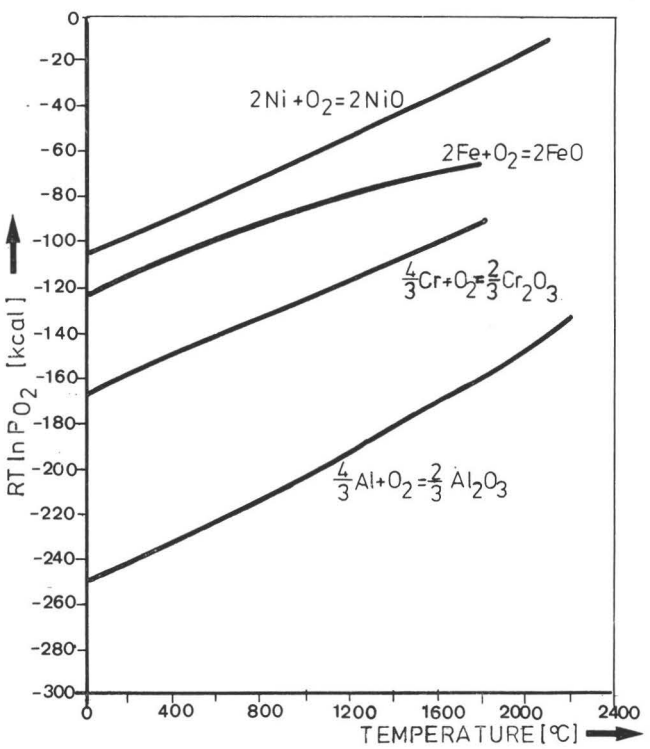

FIG. 1. — *Typical stability diagram for a number of metal oxide systems.*

Now, in practice gas mixtures are frequently not simple, and it is possible to generate low oxygen activity atmospheres by relying on the reaction

$$O_2 + 2\,H_2 = 2\,H_2O \qquad (1)$$

or

$$p_{O_2} = k_1 \frac{p_{H_2O}^2}{p_{H_2}^2} \qquad (2)$$

where k_1 is the equilibrium constant for reaction (1); it is tabulated in many references as a function of temperature. At a fixed temperature it can be seen that the partial pressure of oxygen depends not on the absolute pressures of water vapour and hydrogen, but on their ratio. Again, lines of constant p_{H_2O}/p_{H_2} can be drawn on the Ellingham diagram. Finally, the reaction

$$O_2 + 2\,CO = 2\,CO_2 \qquad (3)$$

can also be used to generate or control oxygen partial pressure:

$$p_{O_2} = k_3 \frac{p_{CO_2}^2}{p_{CO}^2} \qquad (4)$$

and again the oxygen partial pressure depends only on the ratio of CO_2 and CO, not on their absolute pressures. Remember, however, that there may be other limitations: for example on the total pressure, in this case $p_{O_2} + p_{CO} + p_{CO_2}$; locally of course (for example in pores) the conditions may deviate significantly from those in the bulk.

It is important to remember, in connection with these secondary gas-phase reactions, that for calculated oxygen pressures to be maintained the gas phase equilibrium must be attained rapidly: in the case of the oxidation of titanium in $CO - CO_2$ mixtures for example, this is believed not be the case. It is also obviously desirable that the other element involved should not react with the metal: this raises other problems which are dealt with in the next section. Both the metal and the oxide phases are assumed to be at unit activity: if an alloy is being oxidized, or if the oxide activity is altered (for example by reaction with another constituent of the environment, or another reaction product) the lines on the Ellingham diagram will be displaced.

2.2. Pure Metal in a Mixture of Two Oxidants

Again it is possible to represent the situation by a number of equilibria, but the number of reactions may be much more extensive. Thus, for example, in considering the case of pure nickel corroding in a sulphur and oxygen containing environment, the possible reactions may be written as

$$2\,Ni + O_2 = 2\,NiO \qquad (5)$$

$$2\,Ni + S_2 = 2\,NiS \qquad (6)$$

$$2\,NiO + S_2 = 2\,NiS + O_2 \qquad (7)$$

$$2\,Ni + S_2 + 2\,O_2 = 2\,NiSO_4 \qquad (8)$$

$$2\,NiO + S_2 + O_2 = 2\,NiSO_4 \qquad (9)$$

$$NiS + 2\,O_2 = NiSO_4 \qquad (10)$$

In writing equations (5)-(10), the existence of other sulphides has been neglected for simplicity. All the equilibria are well-known, and thus it is possible to determine the partial pressure of oxygen in equilibrium with nickel and NiO, the partial pressure of sulphur in equilibrium with nickel and NiS, and so on. It is now customary to plot the information on a diagram representing regions where given phases are stable: in two dimensions it is possible to do this at a single temperature. There is

some disagreement as to the best variables to choose, but if they are p_{S_2} and p_{O_2}, the partial pressures for reactions (5) and (6), which are then the boundaries between a region where nickel is the stable phase and regions where the oxide and the sulphide respectively are stable, are straight lines parallel to the axes. Similarly, from equation (7) it can be seen that the boundary between the region where the sulphide is stable and the region where the oxide is stable is the line $p_{S_2} = p_{O_2}$, at 45° in the diagram. The complete diagram at 1,200 K is shown in figure 2 (*a*), and the temperature dependence is illustrated in figure 2 (*b*). Diagrams of this kind were first used in studies related to the smelting of ores, but they are clearly useful in studying oxidation reactions.

The same principles can be applied to any number of oxidants, but graphical representation is difficult with three, and impossible with more.

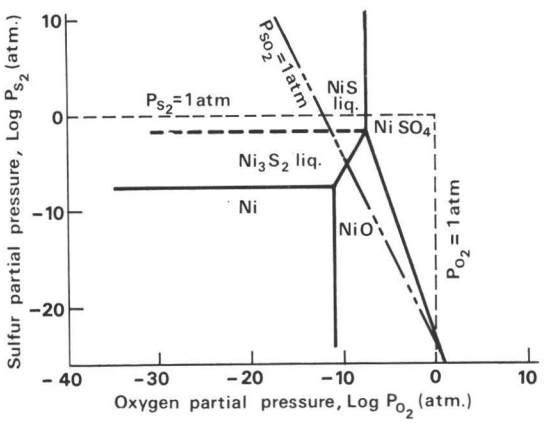

FIG. 2 *a*.

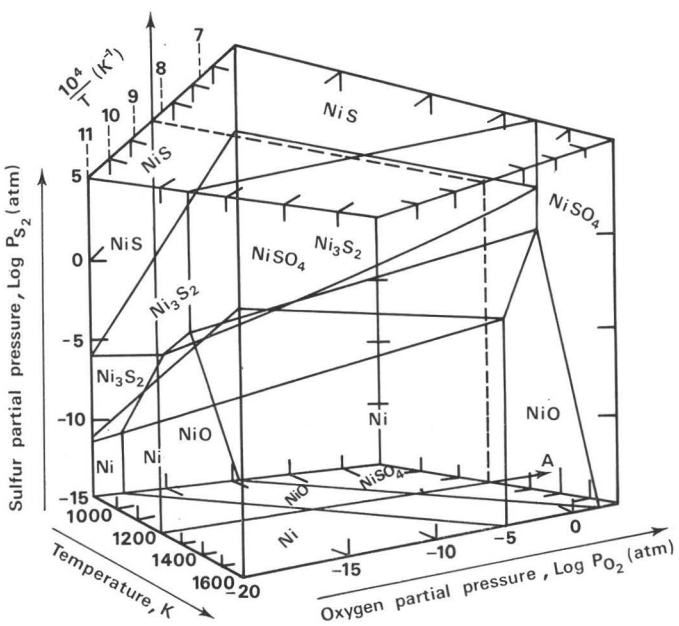

FIG. 2 *b*.

FIG. 2 (a) *Stability diagram for the* Ni — S — O *system at 1,200 K* (from Quets and Dresher, ref. [2]). (b) *Stability diagram for the* Ni — S — O *system at temperatures between 900 and 1 600 K* (from Quets and Dresher, ref. [2]).

As before, the assumption is made that the condensed phases are at unit activity, and this is clearly not always true. For example, if there is extensive solid solubility between two phases, it is clearly not correct to draw a sharp boundary between their stability regions. If the oxidants are reacting with an alloy, or if any of the products reacts with or dissolves in the environment, again the diagrams would have to be modified.

Finally, specification of the activities of the oxidant species in a complex atmosphere may present difficulties. For example, combustion atmospheres may contain CO, CO_2, CH_4, H_2O, H_2, H_2S, SO_2, SO_3, O_2, NH_3, N_2 and possibly others; several simultaneous reactions must be considered:

$$2\,CO + O_2 = 2\,CO_2 \quad (11)$$

$$2\,CO = 2\,C + O_2 \quad (12)$$

$$CO + 2\,H_2O = CH_4 + 1\,1/2\,O_2 \quad (13)$$

$$CO_2 + 2H_2O = CH_4 + 2\,O_2 \quad (14)$$

$$CH_4 + O_2 = 2\,H_2O + C \quad (15)$$

$$2\,SO_2 + O_2 = SO_3 \quad (16)$$

$$2\,SO_2 = SO_2 + 2\,O_2 \quad (17)$$

$$SO_2 + H_2O = H_2S + 1\,1/2\,O_2 \quad (18)$$

and so on. Provided thermodynamic data are available for all the reactions, the calculations are not difficult, but they are tedious; but eventually the chemistry of the atmosphere can be uniquely specified in terms of p_{O_2}, p_{S_2}, a_C, p_{H_2}, p_{N_2} or some equivalent set of variables. This assumes of course that the atmosphere is at equilibrium, and frequently it is not: in the absence of a catalyst the SO_2/SO_3 equilibrium for example, is sluggish. If the gas is flowing quickly in a system where the temperature varies rapidly, quite gross departures from equilibrium can be present, and then in the neighbourhood of a catalyst surface the system may attempt to attain equilibrium, producing locally very high partial pressures. This technique is used in gas-phase nitriding, where NH_3-rich mixtures are passed over hot metal: the local activity of nitrogen at the metal surface can be equivalent to a partial pressure of several atmospheres. In other examples, if circulation is restricted in any parts of the system, local compositional variations can arise: this has been suggested as a mechanism whereby very high carbon activities are produced during oxidation in CO_2 atmospheres, as the gas diffuses through a porous oxide towards the metal surface [3].

Sometimes the information on the stability of phases can be used to suggest the actual activities in the atmosphere near a reacting metal surface. However, whichever way they are used, it is clear that these thermodynamic predominance diagrams are a most important tool. Unfortunately, adequate thermodynamic information for their construction for important practical systems is often not available.

2.3. An Alloy in a Single Oxidant

Most important practical problems are concerned with the oxidation of alloys and from a thermodynamic point of view it is necessary to calculate the oxide phase in equilibrium with the alloy. This is done in a similar manner to the preceeding section and Pettit [4] has

presented an analysis for the oxidation of the Ni — Al system in the range 900-1 300° C which will illustrate the principles.

The following reactions can take place on the surface of the alloy where the oxide phases are assumed to be virtually pure:

$$2\,\mathrm{Al\,(alloy)} + 1\,1/2\,\mathrm{O_2} = \mathrm{Al_2O_3} \quad (19)$$

$$\mathrm{Ni\,(alloy)} + 2\,\mathrm{Al\,(alloy)} + 2\,\mathrm{O_2} = \mathrm{NiAl_2O_4} \quad (20)$$

$$\mathrm{Ni\,(alloy)} + 1/2\,\mathrm{O_2} = \mathrm{NiO} \quad (21)$$

These oxides will all be present as nuclei scattered over the alloy surface shortly after the admission of oxygen, and because of their rapidity of formation they need not be in equilibrium with the alloy. As oxidation proceeds, equilibrium between the alloy surface and the oxide phases is determined by the composition of the alloy at the alloy/oxide interface by the following exchange reactions.

$$3\,\mathrm{NiAl_2O_4} + 2\,\mathrm{Al\,(alloy)} = 4\,\mathrm{Al_2O_3} + 3\,\mathrm{Ni\,(alloy)} \quad (22)$$

$$4\mathrm{NiO} + 2\,\mathrm{Al\,(alloy)} = \mathrm{NiAl_2O_4} + 3\,\mathrm{Ni\,(alloy)} \quad (23)$$

Application of the law of mass action to equation (22) and (23) yields the following equilibrium conditions:

$$\left(a^2_{\mathrm{Al}}/a^3_{\mathrm{Ni}}\right)_{\text{eq. 22}} = \exp.\ \left(4\Delta G^0_{\mathrm{Al_2O_3}} - 3\Delta G^0_{\mathrm{NiAl_2O_4}}\right)/\mathrm{RT} \quad (24)$$

$$\left(a^2_{\mathrm{Al}}/a^3_{\mathrm{Ni}}\right)_{\text{eq. 23}} = \exp.\ \left(\Delta G^0_{\mathrm{NiAl_2O_4}} - 4\Delta G^0_{\mathrm{NiO}}\right)/\mathrm{RT} \quad (25)$$

where a_{Al} and a_{Ni} are the activities of aluminium and nickel, $\Delta G^0_{\mathrm{NiO}}$, $\Delta G^0_{\mathrm{Al_2O_3}}$ and $\Delta G^0_{\mathrm{NiAl_2O_4}}$ are the standard free energies of formation of the respective oxides and R and T have their usual significance. The equilibrium activity ratios can be calculated using free energy of formation data from Elliott and Gleiser [5] and Tretjakow and Schmalzreid [6]; at 900° C from the equilibrium [22], $\left(a^2_{\mathrm{Al}}/a^3_{\mathrm{Ni}}\right)_{\text{eq. (22)}} = 10^{-36.9}$ and at 1,300° C, $10^{-27.7}$. The corresponding values for equilibrium (23) are $10^{-40.8}$ and $10^{-29.2}$. Thus, the activity of nickel is vitually unity and consequently equations (24) and (25) may be written as

$$(a_{\mathrm{Al}})_{\text{eq. 25}} = 10^{-18.5}\ (900^\circ\ \mathrm{C}) \text{ and } 10^{-13.9}\ (1\,300^\circ\ \mathrm{C}) \quad (26)$$

$$(a_{\mathrm{Al}})_{\text{eq. 26}} = 10^{-20.4}\ (900^\circ\ \mathrm{C}) \text{ and } 10^{-14.6}\ (1\,300^\circ\ \mathrm{C}) \quad (27)$$

If a_{Al} at the alloy/oxide interface is greater than that given in equation (26), then Al2O3 is the only stable oxide on the surface of the alloy: reaction (22) proceeds to the right. If a_{Al} at the alloy/oxide interface lies between the values given in equations (26) and (27), $NiAl_2O_4$, the spinel is the only stable oxide, and finally if it is less than the value of equation (27) NiO is the stable oxide. It must be noted that these activities are those at the alloy/oxide interface: these will usually be different from the bulk of the alloy, since a flux of reactant to the interface must be maintained, as will be seen later.

The present thermodynamic treatment is not complete because the oxygen pressure in the gas phase has not been considered. A stability diagram such as that presented in figure 3 can be used. Al_2O_3, $NiAl_2O_4$ or NiO is stable providing the oxygen activity in the gas phase is greater than the equilibrium value defined by the curve for the alloy — Al_2O_3, alloy $NiAl_2O_4$ or alloy — NiO equilibrium, curves [1], [2] and [3] respectively. If the oxygen activity in the gas phase is less than the equilibrium value, no oxide phase is stable on the alloy. The aluminium activities corresponding to equation (24) and (25) are also included in figure 3, and on the basis of activity data in the Ni — Al system [7], these correspond to concentrations of less than 1 ppm.

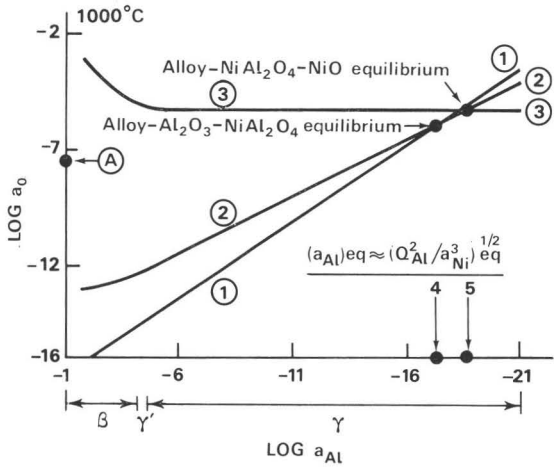

FIG. 3. — *Stability diagram for the oxide phases that can be formed on* Ni — Al *alloys at 1,000° C. Curves 1, 2 and 3 are the alloy-*Al_2O_3, *alloy-*$NiAl_2O_4$ *and alloy-*NiO *equilibria respectively. Points 4 and 5 correspond to the aluminium activities given by equations* (24) *and* (25) *(see text) respectively. The phases along the abscissa correspond to phases in the binary* Ni — Al *system* (from Pettit, ref. [4]).

This treatment illustrates how restricted the conditions are for the formation of the spinel $NiAl_2O_4$, so that in practice one can expect either Al_2O_3 or NiO to be stable; also the amount of aluminium required for Al_2O_3 to be the only stable oxide is extremely small. However, in practice external scales are not formed at concentrations as low as this and thus the thermodynamic approach is not sufficient in itself to predict the oxide that forms. Kinetic considerations, primarily the fluxes of the component metals and oxygen in the oxide and alloy phases, are equally involved as outlined in the next section.

3. KINETICS OF OXIDATION

3.1. Mechanism of Oxidation of Alloys in a Single Oxidant

The thermodynamically stable oxide may not be able to develop a continuous protective layer. To understand this, first consider the steps when an oxide forms on an initially clean surface of a pure metal. There may be absorption and chemisorption steps first, but neglecting these, nuclei of the eventual bulk oxide form on the metal surface, and spread laterally, until eventually the entire surface is covered. Further reaction then involves the transport of one or both reactants through the scale layer, and provided the transport process is independent of scale thickness, the rate of transport, irrespective of the details of the process, should be

inversely proportional to thickness, resulting in a parabolic growth law.

Now suppose an alloy of A and B has such a composition that B_2O_3 is the stable oxide. This may possibly form a complete scale layer, but in order to provide the flux of B required to satisfy the growth law for the scale, a concentration gradient of B must develop in the alloy, the concentration of B at the alloy/oxide interface falling from the initial bulk value. If the steady state surface activity of B falls below that for which B_2O_3 is the stable phase, then on thermodynamic grounds another oxide, perhaps AB_2O_4, will start to form. It is possible for regions of the surface to cycle from B-rich to B-poor, depending on which oxide forms, and a two phase oxide layer will develop. Note that these conditions relate to the transport of material in the scale, the transport of B and A in the metal, and the thermodynamic stability of the phases.

A second possibility however, is that oxygen can diffuse at a significant rate in the alloy, and particles of B_2O_3 form internally. The condition for the transition from internal formation of B_2O_3 to the formation of a continuous external B_2O_3 scale plainly do not involve thermodynamics, since the same phases are present in both cases. It seems likely that it is related to the relative rate of diffusion of B out from the alloy to the surface and the diffusion of oxygen inwards from the surface. Wagner [8] has suggested that the internal oxide particles block the diffusion of oxygen, and thus once the volume fraction of the oxide particles exceeds a critical value, further inward diffusion effectively ceases and an external scale will develop. Attaining the critical volume depends on the atom fraction of B in the alloy, the ratio of molar volumes of B_2O_3 and the alloy, and the extent to which B can diffuse out from the bulk of the alloy as it is depleted by the internal oxidation near to the surface.

Reducing the activity of the oxidant at the surface of the alloy reduces the transport inwards. Thus, the solubility of gases in metals is normally related to the external pressure: for the particular case of oxygen, the solubility varies as the square root of the oxygen pressure (Sievert's law). As a result, for a given alloy at a given temperature, lowering the oxygen pressure increases the tendency for external scale formation.

In practice, even if the alloy has sufficient B for B_2O_3 to be the stable oxide, to provide an adequate flux of B outwards, and to form an external rather than an internal scale, a continuous protective B_2O_3 scale may still not develop, or at least not develop in a reasonable time. This is because when the oxidant is admitted to the alloy surface nuclei of many oxide phases will appear and grow, even if they are not thermodynamically the most stable phase, because initially the system is so far from equilibrium. Thus, in the hypothetical case considered in this section, nuclei of AO and AB_2O_4 would form, as well as of B_2O_3. Now, if B_2O_3 is the optimum protective oxide, it is obvious that the others will grow more rapidly; thus, in practice, the surface will be rapidly covered by (say) AO with isolated islands of B_2O_3 (and possibly also AB_2O_4) at the alloy surface, spreading laterally, both by the direct oxidation process and by an exchange reaction such as those given in equations (22) and (23) for the Ni — Al system.

This sequence is not necessarily less desirable than the direct growth of B_2O_3. The oxygen pressure at the alloy/AO interface is effectively equal to the dissociation pressure of AO, as indicated in the Ellingham diagram, and which is usually significantly lower than that in the external atmosphere, and this can encourage the external formation of B_2O_3. Often indeed the protective B_2O_3 layer can be observed as a « healing layer » developing from an initial internal oxide.

However, in other circumstances the rapidly growing AO can undermine the B_2O_3 nuclei, lifting them away from the alloy surface, so that a two-phase mixture of B_2O_3 particles in an AO matrix forms; later, a solid state reaction can take place converting the B_2O_3 particles to AB_2O_4. In this case, the mechanism can become a steady state process, with no tendency for a protective B_2O_3 layer to form. There is thus a further criterion which is difficult to express in quantitative terms, related to the ability of the stable oxide to form a complete layer without its integrity being destroyed by faster growing, less-stable phases.

3.2. Diffusion during Oxidation

It is evident then from the preceeding discussion, that there is a strong interrelationship between kinetic (diffusion) and thermodynamic aspects of alloy oxidation and one of the most effective means of representing these relationships with the corresponding oxide and subscale structures is by means of a diffusion path on the appropriate A-B-O ternary isotherm. The terms diffusion path, diffusion composition path, and locus of compositions have been used at various times and have essentially equivalent meanings. In the past, this approach to alloy oxidation has not enjoyed widespread use principally because (*a*) until recently there have not been any reliable ternary constitutional diagrams of the A-B-O type (*b*) the principles of multicomponent diffusion theory were not well-established, and (*c*) it has become possible to measure concentration profiles in the alloy and oxide phases (electron probe microanalysis).

Restricting arguments to binary alloys, since with the oxidant this means a ternary system which is the maximum number of components for convenient graphical representation, then during the diffusional-controlled growth of the scale concentration gradients are established in the alloy and oxide phases. It follows from the Gibb's phase rule that the concentration of one of the components is dependent and in general the distributions of the other two components say C_A and C_O, are functions of distance and time. If it can be shown that C_A and C_O are parametric solutions to the diffusion equations, that is both functions of the single variable $\lambda = \times/\sqrt{t}$, then elimination of λ between these expressions will yield a distance and time-independent relation

$$C_A = C_A(Co) \qquad (28)$$

The plot of this relation on the corresponding ternary phase diagram will therefore be stationary with time, and thus represents the diffusion path. Figure 4 shows a schematic diffusion path to illustrate the principles.

Figure 4 (*a*) represents the situation where a layer of oxide AO forms on alloy AB and a depletion of A is produced in the alloy. In the second example, figure 4 (*b*) part of the path cuts across tie lines in the two phase, alloy + AO field, and represents a two phase region in the diffusion structure: internal oxide AO in a B-enriched matrix. A useful summary of the relationship between observed diffusion structures and the corresponding phase diagram has been given [9] and is directly applicable in interpreting oxide structures. Table I [10] is based on that summary and is reproduced here.

TABLE I. — *Diffusion structures and course of diffusion path on corresponding phase diagram.*

Diffusion structure	Diffusion path
Single-phase layer	Traversing a single-phase field.
Two-phase layer	Traversing a two-phase field by cutting tie lines. Ratio of phases indicated by positions at which tie lines cut and equilibrium concentrations by ends of tie lines.
Interface: single-phase-single-phase	Traversing a two-phase field parallel with a tie line. Interface concentrations given by ends of the tie line.
Interface: single-phase-two-phase (two phases altogether)	Traversing the boundary between a single-phase and two-phase field, cutting tie lines in latter.
Interface: single-phase-two-phase (three phases altogether)	Traversing a three-phase field from corner to side, the position on the side being indicated by the two-phase ratio.
Interface: two-phase-two-phase (three phases altogether)	Traversing a three-phase field from side to side, the position on each side being indicated by the corresponding two-phase ratio.

Diffusion path analysis of this type can be used in two ways. Firstly as an aid to interpretation of the oxide structures produced under given circumstances. Figure 5 (*b*) shows an isothermal section of the Ni — Cr — O phase diagram at 1,000º C. The solubilities of NiO and Cr_2O_3 in each other are small although there is also a compound oxide, the spinel $NiCr_2O_4$. The system is very similar to the Ni — Al — O system discussed earlier; points A_1 and A_2 in figure 4 (*b*) indicate the alloy compositions corresponding to the three phase equilibria alloy/NiO/$NiCr_2O_4$ and alloy/$NiCr_2O_4$/Cr_2O_3 respectively. Because of the high stability of Cr_2O_3 with respect to the other oxides, most of the alloy composition range lies adjacent to the two-phase field alloy + Cr_2O_3. Figure 5 (*a*) shows schematically the scale structure produced by oxidation of dilute (< 15 % Cr) Ni — Cr alloys [11]: this has been transposed onto the phase diagram producing the diffusion path $B_1Q_1R_1S_1O$. The system is apparently unstable with respect to NiO — $NiCr_2O_4$: these phases cannot co-exist at a

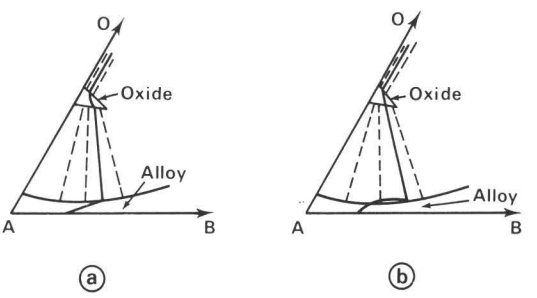

FIG. 4. — *Schematic diffusion path corresponding to the formation of an oxide AO on the surface of an alloy AB. In* (a) *the alloy/oxide interface is planar; in* (b) *it could be irregular, or a zone of internal oxidation, AO in a B-enriched matrix present between the bulk alloy and the superficial oxide* (from Dalvi and Coates, ref. [10]).

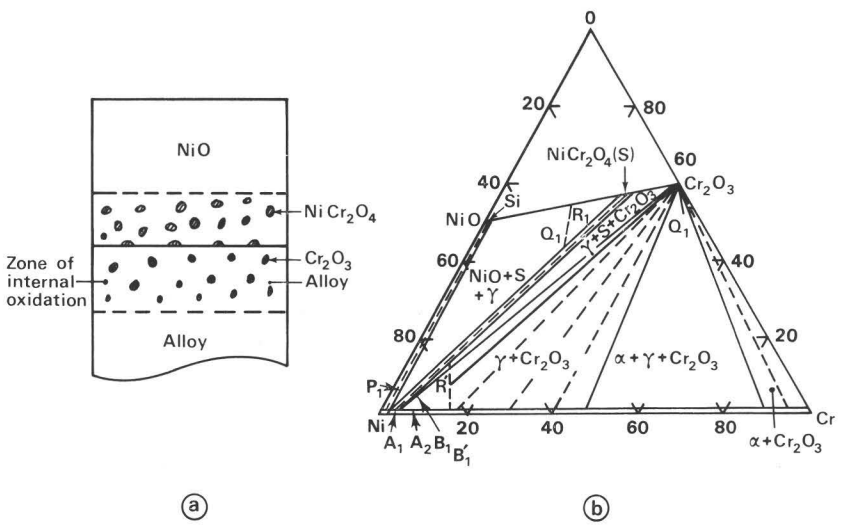

FIG. 5. — (a) *Schematic representation of the scale structure corresponding to the oxidation of a* Ni — Cr *alloy (less than 15* % Cr). (b) *Diffusion paths corresponding to the oxide structures formed on* Ni — Cr *alloys. Point* A_1 *corresponds to only a trace of chromium in the alloy and* A_2 *to less than 1 at.* % Cr. *Solubilities of* NiO *and* Cr_2O_3 *in each other are small and the extent of the spinel phase (near* $NiCr_2O_4$*) is very small. Path* $B_1Q_1R_1S_1O$ *refers to the oxidation of dilute* Ni — Cr *alloys (the oxide structure shown in* (a)*) and* $B_1'R_1'Q_1'O$ *to alloys with greater than 15* % Cr, *corresponding to formation of a single* Cr_2O_3 *layer and a* Cr_2O_3 *internal precipitate in the alloy* (from Dalvi and Coates, ref. [10]).

planar interface, and eventually this leads to the formation of a two-phase zone $NiO - NiCr_2O_4$. The interface between the zone of internal oxidation and the $NiO - NiCr_2O_4$ region corresponds to the dotted line R_1Q_1.

With higher alloy chromium contents, greater than about 15 wt %, the chromium depletion in the alloy is not sufficient to shift the interfacial composition beyond point A_2. Thus, for these alloys the diffusion path is $B_1'R_1'Q_1'O$, corresponding to formation of a single Cr_2O_3 layer and a Cr_2O_3 internal precipitate in the alloy. Again, the diffusion path is an experimental one, corresponding to concentration profiles given by Wood and Hodgkiess [12].

Used in this way, diffusion path analysis only serves as an aid in interpreting scale structures on alloys. However, for any given system, providing the phase diagram were known, and the transport properties of all the various phases had been determined, it would be possible to calculate the diffusion path. This technique would then be predictive, and important information regarding the sequence of phases produced in the scale, the types of oxide, the likely morphology of interfaces, and so on, would become available. Work along some of these lines is currently in its infancy [13].

3.3. Growth Stresses and Oxide Failure

From the preceding discussion, it is clear that a protective, continuous oxide layer is desirable; however, even if it does develop, it may eventually rupture from the metal surface and cease to be protective. Since its formation will have resulted in a metal surface depleted in the element forming the protective oxide, it may be more difficult to re-establish the protective oxide on the freshly exposed metal surface [14]. The failure of the scale can result from a number of causes, of which the most obvious are:

1) The scale growth mechanism results in pores developing at the alloy/oxide interface. This is likely to be the situation if the oxide grows by the transport of the metal ion outwards (rather than the transport of oxygen inwards). These pores will grow as the oxidation proceeds, eventually joining to form large voids; in extreme cases the remaining metal may become almost completely disconnected from the oxide, like a rather small nut in a large shell. This porosity does not itself cause the oxide to cease to be protective, but the mechanical strength of the oxide shell is small without the support of the metallic substrate, and quite small shocks will cause rupture.

2) The scale growth mechanism produces a large growth stress, which eventually becomes large enough to produce rupture of the scale. Growth stresses are known to exist, although there is some argument as to the mechanism responsible for them [15]: in protective oxides the stress system is such that the oxide is in compression and the metal substrate is in tension.

3) The coefficients of thermal expansion of the oxide and the metal differ significantly, and so stresses which can produce oxide failure result from thermal cycling. Generally, the more rapid the temperature change the greater the possibility of damage. « Spalling » on thermal cycling is one of the most serious causes of failure in protective scales.

4) The metallic component is subjected to varying stress systems since the oxide layer is relatively thin, and this contributes little to the overall mechanical strength of the system, in practice the oxide is strained to the same extent as the metal. The fracture strains in oxides are usually small, particularly in tension, and may indeed be less than the elastic strain in the metal prior to yield, so a quite acceptable elastic deformation of the component may result in fracture of the protective scale.

5) The protective oxide is removed by erosion. High velocity dust-laden atmospheres such as might be encountered in systems burning high ash fuels can result in erosion of structural materials, including erosion of the protective oxide. As yet there is little information on the importance of this process, but several programmes are currently studying it.

The failure of a scale need not necessarily be catastrophic. In some cases scales are known to develop cracks but these cracks do not apparently result in enhanced oxidation. Even failures leading to rupture of significant amounts of scale from the surface may not have any effect on the oxidation rate.

Scale failures of no significance in simple oxidation studies can, however, be very important if more than one oxidant is present, since they may allow the access of the second oxidant to the metal; in certain cases this can lead to greatly accelerated attack.

3.4. Breakaway Oxidation

In some cases metals or alloys may oxidize protectively for a long time, but then the oxidation rate accelerates, and may become catastrophic. This type of behaviour is particularly worrying, since it means that the long term suitability of a material cannot be predicted from short term tests. Particular examples are the oxidation of niobium in oxygen at temperatures in the range 300-450º C or so [16]; the oxidation of mild steel in high pressure CO_2 contaminated with H_2O and CO at 350º C [3]; the oxidation of Fe-9 % Cr steels in the same atmosphere at temperatures close to 600º C [3] and higher chromium stainless steels in air or oxygen near to 1,000º C [13]. It is not possible to give a general mechanism for breakaway, but of course the initially protective scale has to lose its protective properties, so a scale failure process is often involved. Thereafter, a new process which does not simply re-form the protective scale is required: sometimes this is the same oxide but in a different physical form, and other times it is an oxide of different composition. Often fragmentation of the metal will be involved, producing an increase in the reaction surface area. It may also result in local temperature rises, since small metal fragments will be less able to dissipate the heat of reaction. In the case of alloys suffering this type of process in CO_2 atmospheres, it seems probable that

changes in gas composition within pores in the oxide eventually result in the deposition of elementary carbon, or carburization of the metal, preventing the formation of a coherent oxide layer. This process combined with the large increase in oxygen potential as the carbon monoxide content is decreased is thought to be responsible for the breakaway process.

Again, the problem is more serious in the presence of environments containing more than one oxidant: the particular case of hot corrosion, where generally acceleration in oxidation rates are related to contamination by alkali salt deposits, will be discussed later.

3.5. The Influence of the Alloy Structure

The large majority of structural alloys are multiphase, and this too can have an influence on oxidation behaviour [18]; however there has been little systematic study of this particular problem. This is, in part, because often the oxidation depletes one or other components in the surface of the alloy so that its composition is displaced into a single phase region: an example of this is the oxidation of Ni — Cr — Al alloys in which the bulk is two phase $\gamma + \gamma'$, but the formation of an external Al_2O_3 scale depletes the outer layers of the alloy in aluminium, and it becomes single phase γ.

Even where several phases are present in the alloy right up to the interface they would presumably be in equilibrium and the activities of all the components everywhere the same. If the activity determines the nature of the oxide formed, it would thus be expected that the same oxide should form over all the phases present. However, even in this case there may well be some effects because the metal surface recedes at different rates over the different phases because of their different volume fractions of the element or elements being removed by the formation of oxide. The irregular interface thus generated may be expected either to result in early scale fracture due to the existence of components of the growth stress normal to the general alloy surface, or possibly in improved scale adhesion due to the arrest of cracks at the alloy/scale interface by the irregularities, or to « keying » of the oxide.

Two examples will serve to illustrate possible effects. In the first, tantalum (similar behaviour also occurs with niobium) when oxidized in certain temperature ranges develops of suboxide TaO_z beneath the metal/Ta_2O_5 interface, so that subsequent oxidation is essentially of a two-phase material: the sub-oxide is stabilised by the growth stresses. Since the tantalum atom density in the suboxide is less than that in tantalum metal, pores develop in the pentoxide above the platelets [19]. The second example concerns the oxidation of a Ni-20Cr alloy reinforced by tungsten fibres [20]. The tungsten oxidizes very rapidly, the large attendant volume increase disrupting the protective Cr_2O_3 scale formed over the matrix, and also disrupting the metal. Rapid oxidation occurs at the matrix grain boundaries and the metal is fragmented.

Catastrophic destruction of the composite follows.

3.6. Some further Practical Consideration

For structural alloys to be used in environments with relatively high oxygen activities at temperatures in excess of 800° C, relatively few oxides will provide adequate protection. On the basis of diffusion data, and oxide growth data, the principal candidates are Cr_2O_3, Al_2O_3 and SiO_2. It is possible that some spinels, such as (Fe, Mn, Ni, Co) (Fe, Mn, Cr, Al)$_2O_4$ would be adequate, but it is virtually impossible for continuous layers of compound oxides to form: particular exceptions are the M_3O_4 types scales formed on iron-based alloys in low oxygen activity atmospheres, but these usually relate to lower temperatures than are being considered here.

SiO_2 scales are seldom used, since there are problems with the spalling resistance: the coefficient of thermal expansion differs significantly from most alloys. However, the refractory metals niobium, tantalum, tungsten and molybdenum have been protected for aerospace application by silicide coatings which form SiO_2 scales in practice: the lifetime required though is short, and the number of thermal cycles which have to be accommodated is limited.

Alloys forming Cr_2O_3 protective scales are common. The early heater alloys based on Ni-20 % Cr are examples: the high chromium superalloys based on nickel, cobalt or iron, all form Cr_2O_3 protective scales. Relatively large amounts of chromium are required to ensure that a Cr_2O_3 scale can be formed and maintained: at least 20 % for nickel, 13 % for iron and 25 % for cobalt; but then usually this is no great disadvantage since chromium is an effective solid solution strengthener and has relatively little effect on the melting point of the alloy. It may however stabilise deleterious intermetallic compounds such as sigma phase. The major problem with Cr_2O_3 scales is that they undergo further oxidation to a volatile oxide, CrO_3; this process can be enhanced in the presence of water vapour. This oxidation is limited by diffusion through a gaseous boundary layer, and thus its rate of formation is a function of the gas velocity: in high velocity environments, such as the gas turbine, this limits the usefulness to temperatures below about 900° C.

Alloys forming Al_2O_3 protective scales are also common: the well known heater alloy kanthal is an early example. In principle Al_2O_3 should be particularly suitable, since its growth rate is very much slower than that of chromia, and it is much more stable; however, in simple alloys much more aluminium is needed to form a stable Al_2O_3 layer than would be expected, and the spalling resistance is not very good. Aluminium is often a less desirable alloying element than chromium forming brittle intermetallic compounds and often lowering the melting point to an unacceptable degree. Fortunately, however, it turns out that the presence of 10 % or so of chromium reduces greatly the amount of aluminium required to form an Al_2O_3 scale: for nickel and cobalt-base alloys to around 5 wt. %, which is usually acceptable on strength grounds. The composition regions where the various oxide phases form in these ternary alloys can be represented most conveniently on an « oxide map » [21] (These are not to be confused with equilibrium diagrams or stability

diagrams presented earlier. The oxide maps present experimental results showing which scale structure is formed over which range of composition. They therefore take into account all the various thermodynamic, and kinetic factors referred to earlier. They are not predictive in the sense that they are obtained from experiment rather than theory, but they do allow some extrapolation between the various measured compositions). Figure 6 and 7 present such maps for the Ni — Cr — Al and Co — Cr — Al systems.

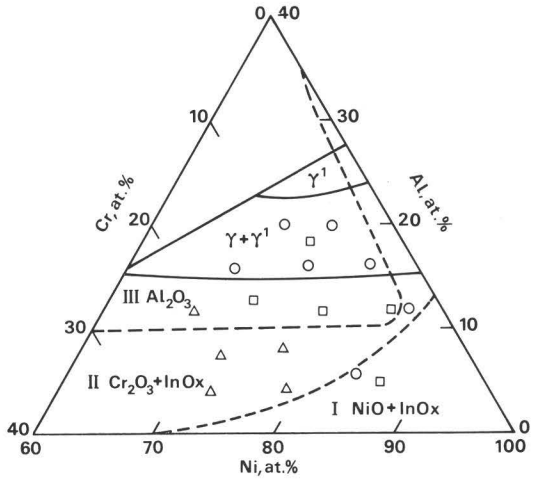

FIG. 6. — *Oxide map for the ternary system* Ni — Cr — Al *at 1,000° C. The points represent data from three different sources (InOx = internal oxide)* (from Wallwork and Hed, ref. [21]).

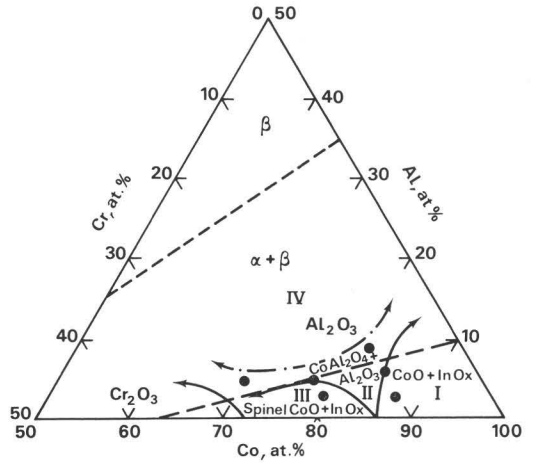

FIG. 7. — *Oxide map for the ternary system* Co — Cr — Al *at 1,100° C* (from Wallwork and Hed, ref. [21]).

The mechanism whereby the presence of chromium reduces the level of aluminium necessary for a continuous Al_2O_3 scale (or for that matter aluminium reducing the level of chromium required for a Cr_2O_3 scale) is the subject of some debate at the moment, but it seems certain that a modified version of Wagner's « secondary getter » model is correct. In this the function of the chromium is to establish a surface oxide and hence a low oxygen activity at the alloy surface which encourages the aluminium to oxidize externally (that is at the alloy/Cr_2O_3 interface) rather than internally. Several nickel-base superalloys owe their excellent oxidation resistance to Al_2O_3 scales, but practically, the most significant demonstration of its protective properties is in the widespread use of aluminium-rich coating for components exposed to elevated temperatures.

For both Cr_2O_3 and Al_2O_3 forming systems, the spalling of the oxide on thermal cycling has proved to be the life-limiting factor in many applications. It was observed, over forty years ago, that the presence of rare earth elements in alloys reduced greatly the tendency of Cr_2O_3 scales to spall from Ni-20 % Cr heater alloys; the source of the rare earth in these modified Nichrome alloys was cerium mischmetal, used for de-oxidation. In the last few years this phenomenon has been widely studied and utilized- the so-called « rare-earth effect ». It now appears that the same result can be achieved with a fine dispersion of the oxide of any reactive metal — ThO_2, Y_2O_3, TiO_2, even Al_2O_3. The dispersion has a number of other interesting effects in addition to that on scale adhesion: most importantly, it reduces very significantly the amount of chromium required to form a continuous Cr_2O_3 scale; in the case of cobalt for example, by a factor of two, to less than 15 % [22]. This appears to be related to the stable oxide particles acting as nucleation sites producing a very fine grained initial oxide, and so reducing the time required for a protective Cr_2O_3 layer to spread over the alloy surface, reducing the tendency for it to be undermined and disrupted by the rapidly growing NiO or CoO. The role of the stable oxide particles in improving the adhesion of the oxide is a matter of some controversy at the moment.

In the case of alloys forming Al_2O_3 scales, a stable oxide dispersion (there are of course, far fewer oxides that are stable with respect to Al_2O_3 than with respect to Cr_2O_3) improves the oxide adhesion, but in Ni — Cr — Al or Co — Cr — Al systems it does not change significantly the amount of aluminium required to form an Al_2O_3 scale. This is not surprising, since in the presence of chromium it is not the physical disruption of the Al_2O_3 which is responsible for determining the amount of aluminium required. It might of course change the amount of chromium required to allow the formation of an Al_2O_3 scale with a limited aluminium content, but this point has not been examined.

Heat resistant alloys normally contain a number of relatively reactive metals which are there for the purpose of improving the mechanical properties, and usually these do not play a very important role in the oxidation process in simple atmospheres. Titanium is sometimes an exception and can be harmful in nickel-base superalloys: relatively rapidly growing islands of rutile, TiO_2, can form over titanium-rich phases, and these can disrupt protective scales. In the presence of complex oxidizing environments, minor alloying elements may play a more significant role.

Metallurgical condition can be significant, mostly in relation to grain size in single-phase materials and to phase size and distribution in polyphase materials (as outlined in the earlier section). Grain size is important

in chromia-forming alloys: smaller grain sizes encourage the development of protective Cr_2O_3 scales earlier, and at rather lower chromium contents, than do large grain sizes. There are two possible effects: the first is that the small grain size increases the chromium flux outwards, allowing the formation of Cr_2O_3 over the grain boundaries which then grow rapidly over the remainder of the alloy surface. Alternatively, recalling that protective Cr_2O_3 layers often appear to be healing internal oxidation regions, the rapid development of Cr_2O_3 along the alloy grain boundaries just below the metal surface due to rapid transport of oxygen inwards is responsible.

At first sight, it might be expected that some alloys would behave even better in low oxygen activity atmospheres, since the formation of the protective external scale should be easier. In practice, however, the situation is more complex than this: it seems likely that the rate of lateral spreading of the protective oxide can be slow, so that the reactive, minor constituents of the system can be oxidized; in particular, oxygen or other oxidants may be able to penetrate down grain boundaries into the bulk of the alloy before the protective scale is complete, and oxidize the reactive elements *in situ*. This could then prevent the protective scale from ever healing over the grain boundaries.

Some metals and materials which are unacceptable in high oxygen activity atmospheres become potential candidates in low oxygen activies. Thus, molybdenum oxidizes to form the volatile oxide MoO_3 at normal oxygen pressures, and the rate of oxidation is very rapid. However, at low oxygen activities, only the lower oxide MoO_2 is stable and this is quite protective. Graphite is also a possible structural material at sufficiently low oxygen activities.

4. OXIDATION OF ALLOYS IN MIXTURES OF OXIDANTS

In principle it would appear that so long as the chemistry of the atmosphere is fixed, the stable compound in equilibrium with the atmosphere should also be fixed in the manner indicated on the thermodynamic stability diagrams given earlier. However, it should be remembered that the activity of all the oxidants within the bulk of the alloy is effectively zero, so there are activity gradients from the atmosphere to the alloy for all the oxidants. Thus, upon the formation of a product phase contiguous to the metal, local equilibria may be set up internally which deviate greatly from the bulk gas composition and thereby allow the formation of less stable compounds. The thermodynamics of these processes have been examined [23, 24]. Again, it is most convenient to represent these variations through the scale structure as a diffusion path on the stability diagram. Thus, figure 8 shows the Cr — S — O stability diagram [35] which is similar to that in the Ni — S — O system referred to earlier. If the activity path starts in the Cr_2O_3 stability region, it can cross into the « CrS » region before it enters the Cr region. If the rate of diffusion of sulphur through the Cr_2O_3 region is slow, then

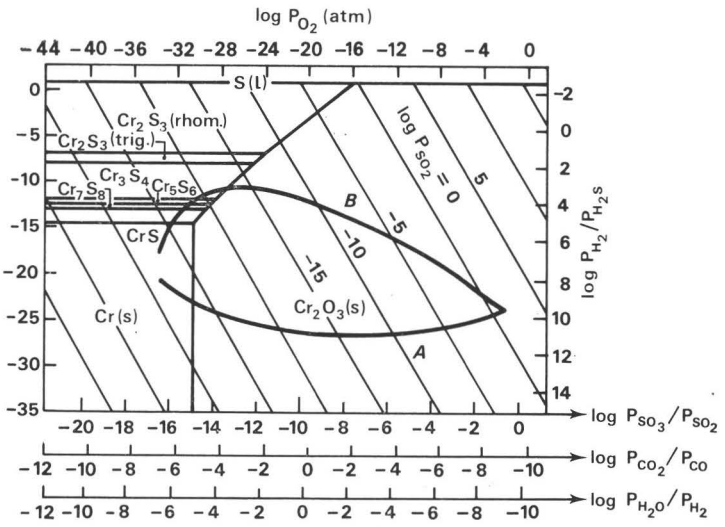

FIG. 8. — *Stability diagram of the* Cr — S — O *system at 1,000 K* (from Rapp., ref. [25]). *Possible schematic diffusion paths have been included. A indicates a situation where no inner sulphide layer would be formed and B the case where an inner layer of sulphide can be expected.*

the inner sulphide layer will be very thin. Currently, however, it is not possible to use these diagrams in a predictive sense as the factors determining the course of the path have not been determined; it does present an exciting challenge for the future.

In practice, there is the additional possibility of fluctuations in the activity of the atmosphere, which may take the system from one stability region to another.

Finally, there are morphological aspects. Thus, for example, if an alloy of Ni-20 % Cr is carburized a two phase alloy consisting of a carbide in an essentially nickel matrix develops. If the mixture is coarse, a Cr_2O_3 scale forms over the carbide and NiO over the nickel. Oxygen is apparently able to diffuse rapidly down the carbide or along the grain boundaries and gradually the carbide is replaced by Cr_2O_3; there are some problems with the rejected carbon, but these will not be considered here. On the other hand if the mixture is fine, the carbide can provide sufficient chromium to form a protective external scale, beneath which is a region depleted of carbide. The actual course of the oxidation thus depends on the morphology of the carbide mixture. Where carburization and oxidation are taking place simultaneously or sequentially, there are clearly similar criteria: the thermodynamic argument is not sufficient in itself.

5. HOT CORROSION

Hot corrosion is the term usually used to describe the accelerated oxidation of iron, nickel and cobalt-based heat resisting alloys which occurs in combustion gases containing small amounts of certain impurities, notably sodium, sulphur and vanadium. The impurities may

arise from contaminants in the fuel or in the air. Salt deposits are most effective in producing accelerated oxidation when they are present as a liquid film on the surface of alloys, although some investigators have expressed the view that condensation of the molten salt was not in fact essential. The nature of the deposit depends of course on the particular system being considered. Aircraft gas turbine engines run on distillate fuels containing virtually no vanadium and the most important source of contamination is salt ingested with the intake air. This is most commonly seasalt and it reacts with the sulphur in the fuel to form sodium sulphate. Marinised gas turbines, which tend to operate at somewhat lower temperatures, around 750° C as opposed to around 900-950° C in the aero-engine, involve higher levels of sea-water contamination, and the salt deposits may well contain substantially higher levels of sodium chloride in addition to sodium sulphate. Vanadium is a common impurity in residual fuel oils and other lower grade fuels, and during combustion produces low melting point ashes, which can again become deposited on blades and other turbine components.

In coal-fired systems, such as conventional electricity generating stations, mixed salt deposits are equally important in producing accelerated oxidation rates of superheater and reheater tubes. Coal combustion products are quite complex: many coals contain as much as 100 ppm chlorine, similar amounts of sodium and potassium, in excess of 3 % sulphur, and often considerable amounts of iron, zinc, vanadium and other metals. All of these are known to participate in high temperature corrosion processes.

The precise mechanism by which the degradation of materials in these combustion product atmospheres and the morphology of the corrosion products, differ occurs of course from system to system, depending on the alloy composition and on the environment. However, there are a number of similarities: some form of breakdown of the normally protective oxide scale is envisaged resulting in corrosion products which typically consist of an outer layer of porous oxide, an inner layer of porous oxide containing metal fragments, a very irregular scale/alloy interface with intrusions of oxide extending into the alloy, sometimes along grain boundaries, and finally a band in the alloy depleted of many of the less noble alloying additions and containing particles of sulphide.

In recent years, substantial efforts [26] have been made in the gas turbine industry to understand the hot corrosion process and it is appropriate to concentrate on this problem in perhaps a little more detail; understanding of other instances of salt-induced accelerated oxidation is not so well advanced.

5.1. Sodium Sulphate-Sodium Chloride Hot Corrosion

As indicated above, there appear to be two stages in the hot corrosion process: an « incubation period » during which there is little or no attack; then after the termination of this period there is a « propagation stage » during which relatively rapid degradation of the alloy takes place. The most probable reason for the incubation period is the initial formation of a protective oxide on the alloy surface, which has to be removed. Several mechanisms have been suggested for the removal of this scale: it may be dissolved by the molten salt or it may be removed mechanically by abrasion, by bending the substrate, or by thermal cycling. It is possible that sodium chloride reduces the scale/metal adhesion, or in some other way accelerates mechanical breakdown. A distinction can be made between alloys protected by Cr_2O_3 scale and those which form Al_2O_3 scales. Al_2O_3 scales seem to be more susceptible to hot corrosion, perhaps because they can be fluxed by both basic and acidic molten salt (see later), although most alloy compositions which have been examined so far have also been low in chromium. However, Al_2O_3 scales grow very slowly, so that they have excellent oxidation resistance in the absence of salt. The hot corrosion resistance of these alloys is thus clearly related to the length of the incubation period, since once corrosion starts, propagation will be rapid.

At present a number of mechanisms have been proposed to describe the propagation stage: not any one mechanism is completely acceptable. However, before discussing these mechanisms a brief examination of the phase equilibrium involved will be helpful.

When a fused salt is deposited on the surface of an alloy, the composition of the salt is usually modified by reaction with the phases on the surface of the alloy. Again phase stability diagrams are the most useful means for demonstrating the possible reactions and interpreting the effects of such reactions on the corrosion of alloys [27, 28]. Figures 9, 10 and 11, thus help to describe the effects produced by Na_2SO_4 on the oxidation of alloys. The approach, however, is generally applicable to any fused salt (*e. g.* Na_2SO_4, NaCl, K_2SO_4, Na_2CO_3, etc.).

Figure 9 shows that Na_2SO_4 can exist over a range of compositions, the compositions being defined by the oxygen and SO_3 activities; other variables such as sulphur activity or the activities of sulphide or oxide ions could equally well have been used. The latter is inversely proportional to the SO_3 activity and is a useful parameter in that it also defines the acidity of salts.

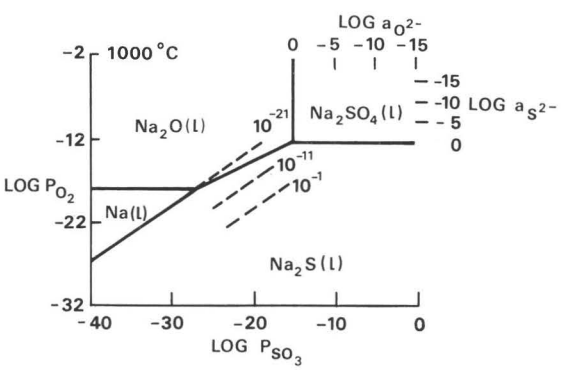

FIG. 9. — *Stability diagram for the* Na — O — S *system at 1,000° C. The oxide ion and sulphide ion activity scales are for the* Na_2SO_4 *region of the diagram. The dashed lines are sulphur iso-activity lines and can be extended over the whole region* (from Goebel and Pettit, ref. [28]).

Fused salts with low oxide ion activities are acidic, whereas those with high oxide ion activities are basic. Both basic and acidic Na_2SO_4 can react with oxides formed on alloys: Figure 10 shows the example of Al_2O_3. At high oxygen ion activities the aluminate ion, AlO_2^-, is stable whereas at low oxygen ion activities the metal cation is stable; for other common oxides, for example NiO, CoO, Cr_2O_3, the corresponding stable ions would be nickelate (NiO_2^-), cobaltate (CoO_2^-) and chromate (CrO_2^-) or the appropriate metal cation.

Point X in figure 10 marks the composition of the as-deposited salt, prior to any reaction with the alloy: it depends on the gaseous environment. Al_2O_3 is stable in this composition regime and can form on the alloy surface. However, its formation causes an oxygen gradient to be established through the deposited salt layer, and the oxygen activity of the salt adjacent to the oxide layer is decreased. This causes the sulphur activity in the Na_2SO_4 to be increased (sulphur isoactivity lines are shown dashed in figure 9 and sulphur can enter the alloy by diffusing through the Al_2O_3 scale. This removal of sulphur from the Na_2SO_4 displaces the oxide ion activity to the left and reaction between the Al_2O_3 scale and the basic salt is then possible. This is basic fluxing. Towards the outer regions of the salt layer, closer to the salt/atmosphere interface, the salt is more nearly stoichiometric (lower oxide ion activity) and the aluminate ions decompose, precipitating the metal oxide as particles which develop into a loose, non-protective scale.

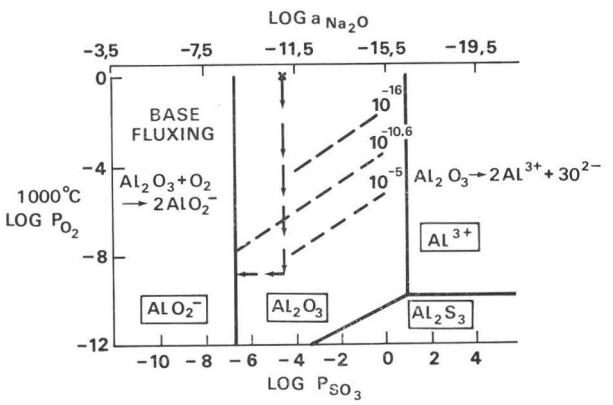

FIG. 10. — *Stability diagram showing the phases of aluminium that are stable in* Na_2SO_4 *at 1,000° C (corresponds to the upper right hand corner of figure 9). The arrows show the composition of* Na_2SO_4 *can change from the as-deposited composition (X) because of removal of sulphur and oxygen. This reaction path is schematic, and in practice likely to be continuous* (from Goebel and Pettit, ref. [28]).

Fused salts can also cause increased oxidation of alloys by an acidic fluxing mechanism. In such cases the protective scales are destroyed because oxide ions from the oxide are given up to the acidic, oxide ion-depleted, salt. Modification of the salt chemistry in this way requires prior reaction with a component capable of forming a stable compound with sodium oxide: examples are molybdenum and tungsten, which can form the stable compounds sodium molybdate and sodium tungstate respectively. This really requires a three dimensional stability diagram, however figure 11 shows a simple projection illustrating the shift of the boundary at which acidic fluxing of Al_2O_3 can occur when Na_2SO_4 contains MoO_3 in solution [29]. Thus the acid salt can dissolve the metal as cations and again these may precipitate and oxidize in the outer, more nearly stoichiometric part of the salt layer. Needless to say, the reaction paths depicted in figure 10 and 11 remain tentative: sufficient data are not available for their complete determination.

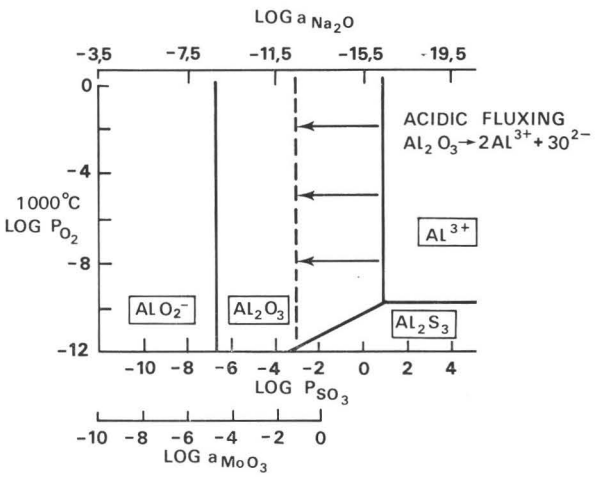

FIG. 11. — *Stability diagram showing the displacement of the boundary (arrowed) at which acidic fluxing of* Al_2O_3 *can occur for the case where* Na_2SO_4 *contains* MoO_3 *in solution* (from Pettit, ref. [29]).

The introduction of sulphur into the alloy, as well as the fluxing processes, can also affect the oxidation rate, and an alternative viewpoint of the hot corrosion process has emphasized the role of sulphur [30]. However, the two mechanisms are not mutually exclusive, and any disagreement may have arisen from attempting to describe the hot corrosion of *any* alloy by *one* mechanism. The differences in behaviour may well be related to differences between severe and less severe environments, and between intrinsically resistant and intrinsically susceptible alloys.

In severe corrosion conditions copious amounts of sulphide are formed, principally chromium-rich networks at grain and subgrain boundaries, and these are then oxidized, so that fingers of oxide extend into the alloy, clearly following the sulphide penetration. Nickel or cobalt-rich particles become isolated and incorporated into the scale. The sulphur released by the oxidation of the sulphides penetrates into the alloy in advance of the oxidation front to form fresh sulphides; as a general rule no sulphur is lost to the atmosphere, so that after initiation hot corrosion will continue without further introduction of sulphur. In extreme cases, the sulphur activity behind the oxide scale can be increased to a level where liquid sulphides develop, resulting in catastrophic destruction of the alloy. This type of salt-induced degradation can be described as a sulphidation/oxidation mechanism [28, 31].

Under less severe conditions, smaller amounts of sulphide are formed, again chromium-rich, as small discrete particles within the alloy. This form of corrosion occurs principally in Al_2O_3-forming alloys, and the sulphidation has the effect of depleting the matrix in chromium. As a result, instead of the aluminium oxidizing as an external, protective layer, it oxidizes as discrete internal particles, and thereafter the matrix can oxidize rapidly. The sulphide particles are again oxidized, but since they are discrete, it appears less easy for the released sulphur to penetrate into the alloy, and some sulphur is liberated as sulphur oxides; continued propagation may then require a continuing supply of condensed salt.

Resistance to sodium sulphate/sodium chloride attack seems to require high chromium contents: in the case of nickel-based alloys, 15 wt. % Cr or more. A graph of corrosive attack versus chromium content [32] for a number of alloys is shown in figure 12. Similar graphs have been presented by other workers [33] although the ratio of chromium to aluminium and titanium contents was thought to be the important parameter. Al_2O_3-forming alloys are generally more susceptible to catastrophic attack under severe exposure conditions than Cr_2O_3-formers. Presumably this is related to the amphoteric nature of Al_2O_3 referred to earlier. Under less severe conditions aluminium additions are reported [34] to markedly increase the corrosion resistance, titanium and cobalt increase it slightly, tantalum has no effect, and tungsten decreases it slightly. Molybdenum additions are increasingly detrimental as the temperature is raised, and may well account for the poor corrosion resistance of IN713 (12.5 % Cr, 6.1 % Al, 0.8 % Ti, 4.2 % Mo, 2.5 % Fe) which has a higher molybdenum content than many typical alloys.

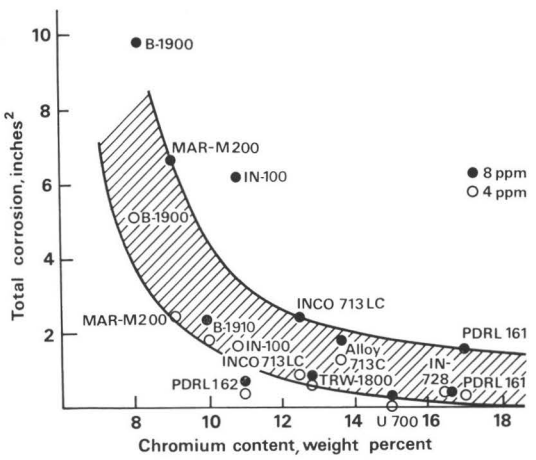

FIG. 12. — *Total corrosion as a function of chromium content for alloys rig tested using JP-4R fuel* (from Walters, ref. [32]).

The idea that the effects of alloy elements can be treated independently is plainly unreasonable, and Stringer [35] has recently published a comprehensive review of hot corrosion behaviour of a wide range of commercially available alloys.

It is generally believed that cobalt-based alloys are rather better than nickel-based alloys under hot corrosion conditions, but again the critical factor appears to be the level of chromium in the alloy. Wheatfall [36] in examining the problem recently, concluded that the evidence suggested that the effect was not intrinsic. This implies that explanations based on different diffusivities in cobalt and nickel or the differing melting points of the respective sulphides are incorrect, and incidentally clearly suggests that in fact formation of liquid sulphides may not in general be particularly important in hot corrosion.

The effect of temperature on the rate of attack is complicated by the interdependence of several parameters. At low temperature, where the salt deposit is solid, some internal sulphides may be formed, but the oxide scale is compact and the rate of attack is relatively slow. The temperature at which catastrophic attack commences generally occurs near the melting point of the salt or the salt mixture. As the temperature is increased further, the rate of diffusion-controlled growth processes increases and hence the rate of attack increases to a maximum, typically around 980º C (fig. 13).

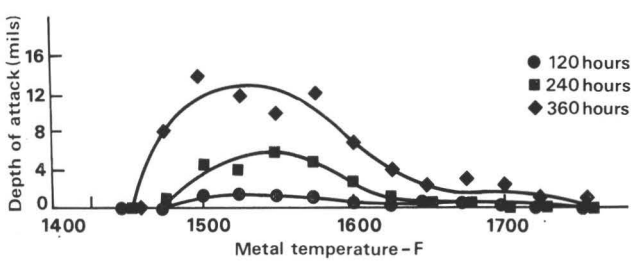

FIG. 13. — *Total corrosion as a function of temperature for IN713 tested using JP-4R fuel with a salt/air ratio of 4 ppm* (from Walters, ref. [32]).

The dew point of Na_2SO_4 in the environment depends on the concentration of ingested salt and the total pressure: typically it is around 900-980º C. At higher salt concentrations the dew point, and hence the temperature range where hot corrosion is likely extends to higher temperatures. With increasing temperature, less and less salt can deposit and hot corrosion attack is replaced by simple oxidation, and the protective oxide scales can again develop.

5.2. Vanadium-induced Hot Corrosion

As indicated earlier, vanadium is present in lower grade fuels, and during combustion produces low melting point ashes in which V_2O_5 is the principal constituent. In these cases the as-deposited ash or salt may be sufficiently acidic to allow acidic fluxing of many of the oxides likely to be found on heat-resistant alloys. However, the extent of attack is enhanced by a variety of additions. The addition of Na_2O increases the rate, and it is genrally reported that the maximum rate occurs at a composition $Na_2O - 6\ V_2O_5$; the addition of Na_2O increases the basicity of the oxide and thus increases its ability to dissolve acidic oxides. Further-

more, the melt changes from an *n*-type semiconductor into an ionic conductor and reduces its viscosity, both of which factors may increase the transport of oxygen in the melt. Na_2SO_4 also increases the rate, and in some cases the rate may be ten times as high as that with V_2O_5/Na_2O mixtures. With a few alloys, a further increase may be obtained by adding NaCl, but in other cases it makes little difference.

A rotating disc method has been used to study corrosion in vanadium-rich melts [37] and it was concluded that the formation of Cr_2O_3 or Al_2O_3 protective oxides reduced the corrosion rate: a high chromium alloy (50 % Ni-50 % Cr) was particularly resistant to attack, although under some circumstances breakaway reactions could be induced, and it was sensitive to small amounts of chloride. In other circumstances [38] alloys based on intermetallic systems Ni_3Al and NiAl (Al_2O_3-formers) were particularly susceptible to V_2O_5 corrosion.

Lower grade fuels containing appreciable amounts of vanadium invariably also contain substantial sulphur impurity contents, and sulphidation/oxidation type attack is also observed. Möller [39] corroded Nimonic 80 A and S 590 (24.4 % Fe, 20.3 % Ni, 20.4 % Cr, 20.1 % Co, 4.1 % W, 4.2 % Mo, 3.9 % Nb, 0.4 % C) for 100 hours in the temperature range 650°-750° C, burning a distillate oil with 0.3 % S as a basic fuel and adding varying amounts of vanadium, sodium and sulphur as oil-soluble compounds. In the most extreme case the fuel contained 2.2 % S, 37 ppm Na and 28 ppm V. The presence of sodium and sulphur alone in the fuel accelerated the attack of S 590, the effect being most marked at lower temperatures: Nimonic 80 A was essentially unaffected. Sulphur and vanadium alone produced a marked enhancement in the oxidation of both alloys, and in fact the addition of sodium alone seemed to make little difference.

It is clear that synergistic effects of different fuel impurities will require a great deal of further study, and the real situation in complex low grade fuels may be very difficult to understand. There is little work available on the relative effects of alloying elements, but it seems probable that high chromium alloys will have the best resistance to fuel-ash attack.

6. *CONCLUSIONS*

The discussion presented in the preceeding sections has attempted to identify the present state of knowledge of high temperature corrosion processes and it is appropriate in this final section to examine briefly the current position with regard to future possible material problems in high temperature environments. In the solution of any problem there are two possible approaches to be followed: one is an empirical approach in which alloys with improved resistance to high temperature attack, or methods to nullify the agressive nature of the environment (for example additives in the case of fused salt attack) are intuitively developed. The other approach utilises basic research to help determine the solution. There are of course many examples which can be quoted to show that the former approach can be very productive, but it does not permit the accumulation of basic data that are required for efficiently resolving the problem. It has been said that most of the oxidation-resistant alloys were developed intuitively, and it is only over the last decade that theory has caught up with practice such that it would now be possible to design an alloy for oxidation resistance from basic principles. It is probably equally true to say that an understanding of corrosion in the presence of condensed layers of fused salts is one step behind this. It is therefore believed that both basic and empirical approaches should be employed concomitantly.

In gaseous high temperature oxidising environments the situation is relatively clear: for adequate resistance to attack an alloy must be able to form and maintain a protective oxide; it is better if this is a simple binary oxide, since the conditions for forming it are less restrictive than for compound oxides. The major candidates are Cr_2O_3, Al_2O_3, and possibly, SiO_2. Thermodynamic analysis, in the form of phase stability diagrams, and considerations of the transport of reactants and alloying elements through the scale and alloy in diffusion path analysis, are currently at a stage at which they are able to provide a fundamental interpretation of many of the observed phenomena. However, there are no *a priori* reasons why these analyses should not be predictive, and future studies would be well directed towards the acquisition of more basic data: these would include the effects of cation and anion activities on the defect structures of mixes oxide systems, the variation of cation activities with composition, and the functional form of the concentration dependence of the diffusion coefficients of the mobile species in the scale. Data on the shape of the oxygen solubility curves for various alloy systems are also highly desirable.

In addition to the above « chemical » factors, « mechanical » factors can also affect the interaction between an alloy and its environment: factors such as the phase constitution and distribution of the alloy, whether the material is under stress or not, thermal stresses, temperature fluctuations, the adhesion of the scale to the substrate, growth stresses in the scale, have been identified in the present discussion. Most unexpected failures of metallic components due to high temperature oxidation have been attributable to one or other of these latter factors, where the protective scale has suffered irreperable breakdown. Unfortunately, they are less amenable to a basic interpretation, and any new developments will therefore rely very heavily on empirical testing programmes.

The position with regard to fused salt corrosion of alloys is less viable. Partly this is due to the increased number of possible salt contaminants which can be involved, and partly due to the added inherent complexity of the processes. In any given application it is important to determine the composition and amounts of fused salts to be deposited on alloys, together with the type of degradation that they produce. It is not necessary to attempt to describe the approach that the empirical work might take. It is necessary, however,

that such effort should be coordinated with more basic studies. Typically the following seem essential: thermodynamic data for the relevant fused salt systems; transport properties of the fused salts; the molten salt chemistry of the relevant systems and the types of reactions that can take place between the fused salts and the protective oxides formed on alloys. These then help to establish definitive models to describe the corrosion of alloys and demonstrate the effects of the various environmental and alloy compositional variations.

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* *

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Rev. int. Htes Temp. et Réfract., 1977, t. *14*, pp. 21-27

ROLLS ROYCE 1971 LTD.
BRISTOL ENGINE DIVISION
Bristol (England)

HIGH TEMPERATURE PROTECTIVE COATINGS FOR GAS TURBINE ENGINES. CURRENT PRACTICE AND FUTURE REQUIREMENTS

By

R. G. UBANK

INTRODUCTION

In a typical gas turbine, air is ingested from the atmosphere and compressed, in doing so its temperature rises to approximately 400° C. The air then passes into a combustion chamber, where vaporised fuel is mixed with the high pressure air and burnt. Gas turbines operate with a wide range of fuels from natural gas and high sulphur diesel fuel, to the highly refined aero kerosene, but always have a high air to fuel ratio; so the combustion gases are highly oxidising with flame temperatures of the order of 2,000° C. These gases are then fed through successive rows of guide vanes and rotor blades, depending on the number of stages in the turbine.

The turbine blade section converts the thermal energy applied by the combustion into work (mechanical energy) and therefore must withstand the full potential of the hot gases from the combustor. The role of coating is to maintain the integrity of these blades and their guide vanes over extended periods.

Blades for advanced engines are now air cooled and almost invariably cast and this allows the incorporation of intricate cooling passages to maximise the air-metal interaction and lower the metal temperatures by 200-250° C.

The nozzle vane is normally arranged to have a low stress to assist it to withstand thermal cycling and heat corrosion in the range 950-1,150° C, whilst the turbine rotor blade is relatively highly stressed by the C. F. load and also has to withstand thermal cycling gas bending and fatigue stresses in the temperature range 800-1,050° C. The lower temperature would be for industrial long life engines and the upper temperature for shorter military aero engine lives.

Conditions in advanced aero engines are now so demanding in terms of power/weight ratio and life, thaf we have to push the limits of material properties at hard as possible. In the case of blades, this consists os mating coatings and advanced superalloys, so that the materials system becomes a viable entity for component application. This tailoring of materials is a continuing process, because the materials in a gas turbine operate in an environment of dynamic change, *i. e.* higher temperatures and longer life and the aim is the highest quality reliability and cost effectiveness.

The improvement in cast superalloy temperature capability, has not been spectacular in the past 10 years; the biggest step forward has been in the introduction of directionally solidified superalloys, showing a 25° C temperature improvement over conventionally cast alloys. Steady progress has however been occurring, improving the hot corrosion behaviour of turbine superalloys.

The varied roles of gas turbine engines, also effects the choice of coating. In high altitude flight, the air is pure and corrosion is primarily of an oxidation type (fig. 1) whereas in a marine service role, the ingestion of sea salt, even in minute quantities, causes a very severe form of hot corrosion. Figure 2 illustrates this and the improvement to be gained by aluminide coating.

In V/STOL aircraft, a severe cyclic service is demanded and in this instance thermal fatigue is the major failure mode.

COATING FAILURE MECHANISMS

Coating failure therefore occurs by several mechanisms.

1. Erosion.

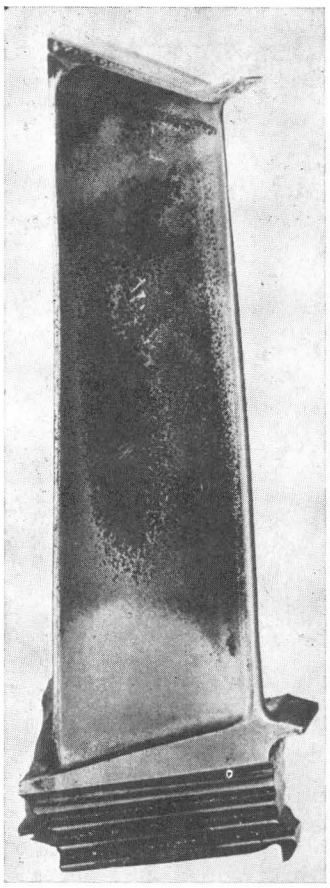

FIG. 1. — *Turbine blade from aero service showing characteristic low growth rate sulphur contaminated oxidation attack.*

2. Mechanical damage from strains of a thermal origin.
3. Interdiffusion with the substrate.
4. Surface loss by corrosion.

The manner in which coatings have developed to meet these demands will now be discussed.

Erosion

Engineers are aware of a carbon particle erosion problem and much effort is directed towards improved burners, to ensure complete combustion and minimise this problem. Erosion from ingested dust however, is still a problem; particularly with the long lives expected of blading in land based engines. Although coatings are hard at ambient temperatures, they are not at elevated temperatures. Some turbine operators, have found benefit from the inclusion of alumina particles in aluminised coatings; to counteract this problem. However, in general this aspect of coating wear-out has not attracted much research effort, but is nevertheless very important.

Mechanical Damage

The application of coatings should not degrade the mechanical properties of the substrate and generally, provided the coating heat cycle is arranged to be compatible with the heat tratment cycle of the superalloy being coated and the coating has adequate ductility, the substrate properties are not seriously affected in creep.

Crack damage in coatings from repeated cycles of thermal strain (thermal fatigue) however, is a life limiting problem in many engines and results from a basic ductility inadequacy in the coating. Once cracks have initiated; they not only lead to mechanical fatigue propagation, but of course allow a path for corrosion gases into the substrate, undermining the coating (fig. 3).

The most widely accepted protective system in current use is the pack diffused aluminide coating, the outer layer of this conversion coating, consists of β NiAl in which the entrapped substrate elements *e. g.* chromium and molybdenum have been rejected in the form of fine precipitates.

This NiAl phase is brittle at room temperature and like all body centred cubic phases, exhibits a brittle-ductile transition change; in this instance, at elevated temperatures as shown in figure 4. The transition temperature is dependent on the aluminium content of the NiAl phase, which has a wide stoichiometric range and for this reason aluminide coatings are frequently diffused after processing, to produce a lower aluminium and gain an improvement in ductility. Fortunately, turbine operating temperatures are above the brittle-ductile transition temperature and these coatings have generally provided an excellent palliative for hot corrosion. However, under some engine conditions involving severe thermal transients, high strains can occur in the brittle temperature range, which results in straining the coating beyond its ductility limit, causing cracking (fig. 5). The design of turbine blades and venes, must therefore take into account these aluminide coating properties, or adopt more ductile overlay coatings.

The thermal fatigue behaviour of aluminide coatings may also be affected by their mode of formation, which has a controlling influence on the structure obtained. Coatings formed at high aluminium activity (inward diffusion type); are fine grained, precipitate strengthened and more resistant to thermal fatigue, than those formed at low aluminium activity and prolonged heat cycles. In this latter mode the outward diffusion of nickel predominates and results in a coating with a low strength pure NiAl phase and a weak columnar grain structure.

Interdiffusion

The development of diffusion barriers is a formidable problem, because of the parallel requirement for a strong metallurgical bond which necessitates ensuring that expansion compatibility, chemical stability and structural integrity are satisfied. From a consideration of the activation energy for diffusion, it can be shown that $Q \cong .38\ T_m$: consequently, the high melting point elements may be expected to offer resistance to interdiffusion.

The refractory metals are particularly attractive for this purpose and one novel example of their use is in the Ta — Cr — Al coating system developed by O. N. E. R. A. In this process, tantalum is used as a precoating to a chrome-aluminising pack diffusion

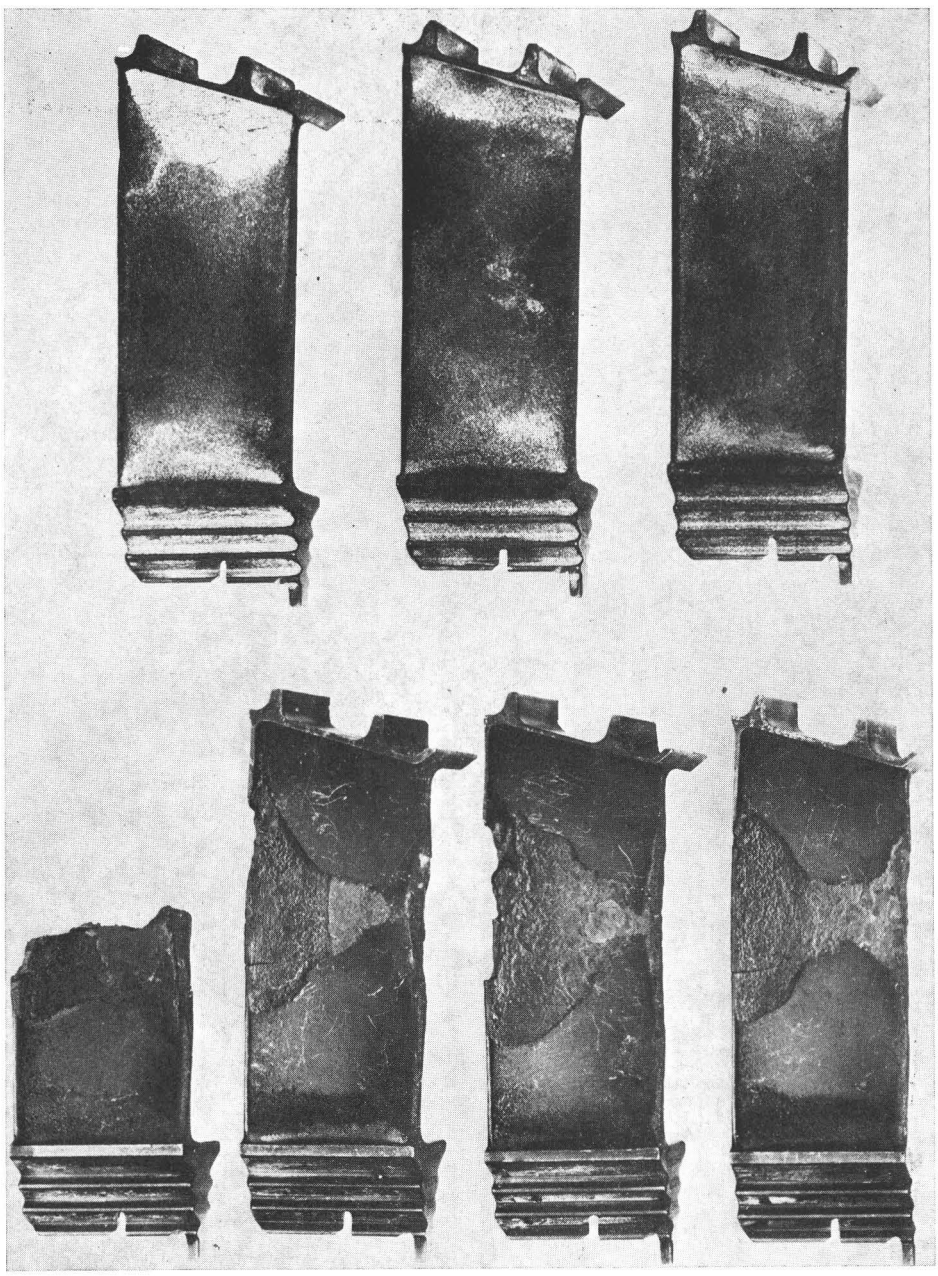

FIG. 2. — *Bottom row: Uncoated turbine rotor blades from marine service showing severe salt corrosion attack. Top row: Unattacked aluminised blades at the same life.*

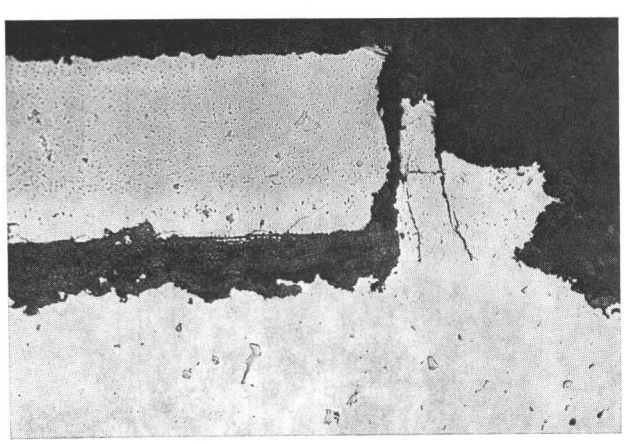

FIG. 3. — *Showing corrosion attack at the interface spreading from cracks in the aluminide coating.*

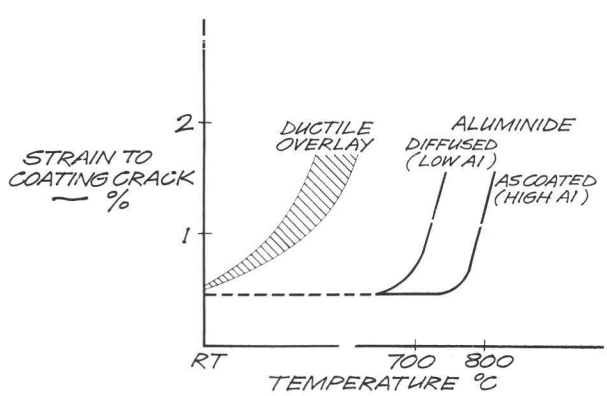

FIG. 4. — *Schematic illustration of brittle-ductile transition behaviour of aluminide and more ductile overlay coatings.*

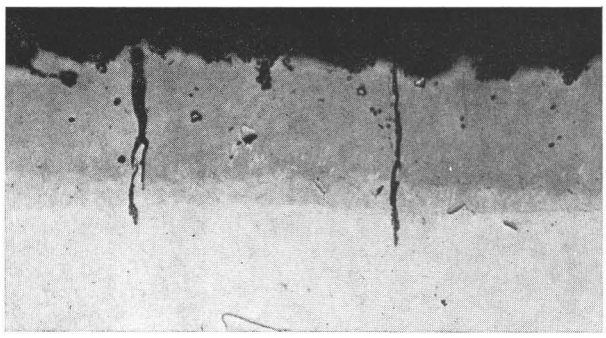

FIG. 5. — *Showing cracks in an aluminide coating as a result of straining beyond its ductility limit.*

treatment. As the aluminide coating forms by diffusion of nickel from the interior, the slower diffusing species tantalum and chromium, are distributed in depth, to form a barrier layer of ~50 % refractory elements content beneath the coating, which acts as a diffusion barrier preserving the protective NiAl outer layer.

An alternative approach is to use the principle, that the terminal phases in a two phase alloy system are in equilibrium at any one temperature and do not interdiffuse. For example, in the CoCrAl system, it is known that a chromium rich phase approximating to $Cr_{23}C_6$ is in equilibrium with β CoAl. In practice however, although effective as a barrier, the bond is weak and delamination of the coating readily occurs with repeated thermal strain cycles.

The number of satisfactory coating/diffusion barrier systems identified is limited, the reason is understandable; however, contrary to common belief; the aluminium losses from interdiffusion of the NiAl coating and the substrate are small at normal turbine operating temperatures, compared to the losses at the surface due to oxide spalling. Work on the barrier coating approach has therefore been deferred, until the spalling resistance of the protective oxide film has been significantly improved.

Surface loss by corrosion

It has been established by many workers that the development of alumina scales are more protective than those based on chromium oxide or spinels; particularly in oxidising conditions and at the higher temperature and gas velocities of turbine engines.

In these oxidising service conditions, the alumina film is continuously but relatively slowly subjected to a damage and repair sequence. However, in sulphidation attack, when sulphur in the form of a sulphate compound or from the fuel and ingested salt are present in the combustion products; the breakdown of the alumina film produces reactions other than the reformation of the alumina film. This allows a catastrophic loss of aluminium and chromium, resulting in a greatly reduced protective life. These corrosion mechanisms have been the subject of extensive work and the theories developed are still controversial.

To enable a long protective life to be obtained from the alumina film a large reservoir of aluminium in the surface layers is necessary; to continuously replace that lost at the surface by oxide spallation.

One of the least costly and most reliable means of achieving this on turbine superalloys, is by a single pack aluminising treatment, in which levels of 20-30 % Al can be obtained.

A great deal of research effort has been expended over the years to modify the aluminide coating with minor amounts of *e. g.* Si, Fe, Ti, Cr; in an endeavour to improve the protective ability of the scales formed and in turn the hot corrosion and oxidation behaviour; but with little reward in terms of life improvement. These researches have established; that for pure oxidation protection the essential need is for a high aluminium content, but for optimum sodium sulphate corrosion resistance, an adequate reservoir of chromium in the aluminide coating is also essential: as this element is continuously lost to the salt deposit at the surfaces.

Since aluminide coatings are conversion coatings, the properties developed are strongly influenced by the chemistry and structure of the substrate and the presence of *e. g.* carbide intrusions into the coating will degrade the corrosion performance (fig. 6). Although there has been little development in superalloy strength potential in the last 10 years, there has been a considerable improvement in hot corrosion performance without loss of creep strength. As would be expected, this has been brought about by an increase in the chromium levels combined with a better understanding of the behaviour of the solution strengthening elements and the precipitation hardening mechanisms. Table I gives the composition of two such alloys IN 792 and IN 738 and compares them with the older IN 100 superalloy.

Fortunately these base alloy improvements have involved higher chromium contents and this has brought about a significant improvement also in the aluminide coated hot corrosion performance. One example of these developments in IN 792 which has

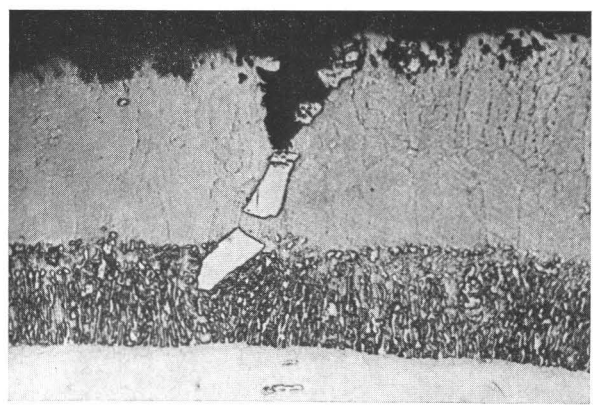

FIG. 6. — *Showing selective attack at a carbide outcrop in the aluminide coating.*

NOTE : For the purpose of this paper the term oxidation refers to conditions with no contaminants and hot corrosion refers to conditions with sulphate compounds or salt contaminants present.

TABLE I. — *Some modern superalloy compositions.*

	C	B	Zr	Cr	Ni	Co	W	Ta	Mo	Ti	Al	Cb
IN 100	0.17	0.015	0.10	10	Bal	15.0	-	-	3.0	4.5	5.5	—
IN 792	0.13	0.013	0.10	12.5	Bal	9.0	4.0	4.0	1.9	4.0	3.5	—
IN 738	0.17	0.01	0.10	16	Bal	8.5	2.7	1.8	1.8	3.5	3.5	0.9

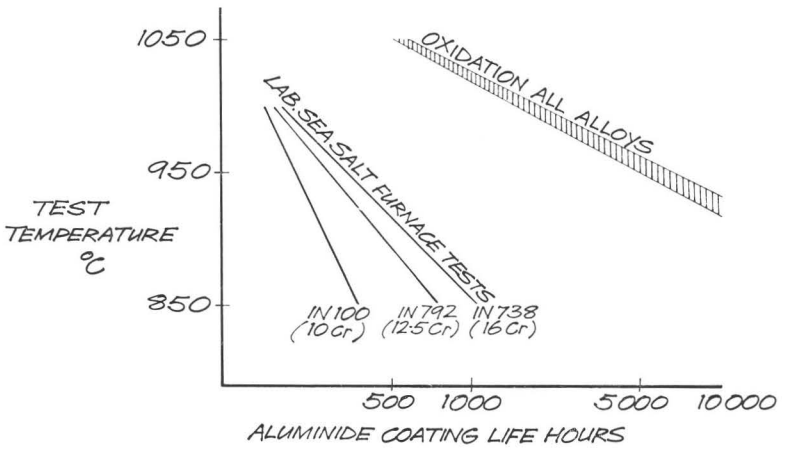

FIG. 7. — *Effect of higher chromium in modern superalloys on aluminide coated hot corrosion life and the dependence on aluminium for oxidation life.*

a similar strength level to IN 100, but with 2.5 % more chromium and superior hot corrosion resistance. Figure 7 shows the dependence on Cr for aluminide hot corrosion resistance and on Al for oxidation resistance.

HIGHLY ALLOYED ALUMINIDE COATINGS

Chromium-Aluminium

This duplex coating involves enriching the surface with chromium by a pack diffusion process, then subsequently converting the enriched layer to aluminide by a conventional pack aluminising treatment. This process enhances the general level of chromium in the coating (fig. 8), and is particularly beneficial on low chromium superalloys < 8 % Cr content to provide adequate hot corrosion protection.

Platinium-Aluminium

In this process developed by D. E. W. of Germany a layer of platinum is applied first by electroplating and then followed by a conventional pack aluminising treatment. The as treated coating figure 9 has approx. 50 % Pt in the surface layers, however this decreases considerably in service as the platinum disperses throughout the coating.

This Pt — Al coating has excellent long term stability, offering a X 3 improvement in oxidation life. The mechanism responsible is not throroughly understood yet, but the platinum does not form an interface barrier; its action is likely to be one of limiting the supply of aluminium to the surface for repair of the protective alumina film.

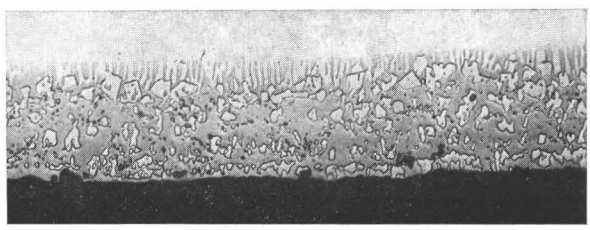

FIG. 8. — *Section through a duplex* Cr — Al *coating showing enchanced chromium content in the form of a coarse precipitate.*

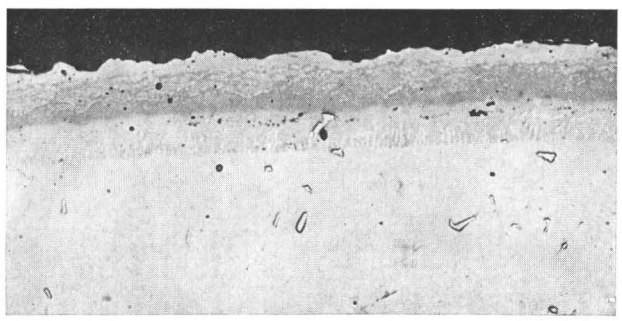

FIG. 9. — *Showing typical structure of a* Pt-*aluminide coating. Light coloured phase at the surface contains 50* % Pt.

Unfortunately this coating has one major disincentive; its high cost, however this remarkable improvement in oxidation life is evidence of the sizeable benefits to be gained from research into surface corrosion mechanisms.

Summarising, the situation on aluminide coatings is that the interaction of all the parameters of the process do not allow for complete control of the chemistry and microstructure. The coating is therefore a compromise in alloy content and relatively brittle because of the high aluminium content. There are also drastic changes in alloy composition at the interface transition zone which can produce undesirable low incipient melting point phases. A further disadvantage is that the critical turbine blade wall section is partly consumed in its formation and this limits the number of times the blade can be refurbished.

It was to overcome these problems and break away from the straightjacket of pack aluminide coatings that serious work on overlay coatings began.

The properties required in the overlay alloy were:

a) adequate ductility to minimise foreign object damage and satisfy cyclic life requirements;

b) good hot corrosion (oxidation performance with laminar attack fronts);

c) low surface spalling tendencies;

d) long term stability and compatibility with the substrate.

OVERLAY COATINGS

Since coatings of this type are added layers to the surface they have the immediate advantage of eliminating the problem of carbide outcrops and low incipient melting point phases.

These overlay coatings are normally based on the NiCrAl and CoCrAl systems and the Al level is balanced to take advantage of alumina protective scales and to provide the required amount of ductility.

Alloys designed primarily for oxidation resistance have Cr levels of 18-20 % whilst for maximum hot corrosion resistance these Cr levels are generally higher in the range 25-40 %.

The importance of cyclic protection has already been stated relative to accelerated corrosion through cracks in the coating. However, greatly accelerated corrosion can also occur due to thermally induced spalling of the protective alumina layer. This effect when repeated over a number of cycles causes aluminium loss at a much faster rate than under isothermal conditions, clearly an improvement in oxide adherence was the solution required.

For many years the benefits of yttrium additions on oxidation resistance has been known, only comparatively recently has this element been added to alumina forming nickel and cobalt base alloys systems (United Aircraft patent). As is now fairly well known the addition of a fraction of a percent of yttrium and other group 111B elements markedly improves the cyclic oxidation behaviour, whilst having only a small effect on isothermal oxidation behaviour (fig. 10). The mechanism by which this improvement occurs is not fully understood and a great deal of rewarding research remains to be done in this area.

Again the resistance to heavy sodium sulphate deposits is primarly affected by the chromium content and yttrium stabilised alumina films offer little additional advantage against this severe form of hot corrosion. New coating alloys to satisfactorily combat this are urgently required.

COATING PROCESSES

Aluminide Coating

The halide activated aluminide coating process is well established and despite its disadvantages will be in use for many years yet. The processing details have been extensively covered in the literature and need no further elaboration here, except that with improvements in turbine technology; service lifetimes are now in many thousands of hours and it is becoming more important now to coat internal cooling passages. Process development in this area is required in the future.

OVERLAY COATING PROCESSES

Various methods are available but the vacuum deposition route is the most advanced production technique available (fig. 11).

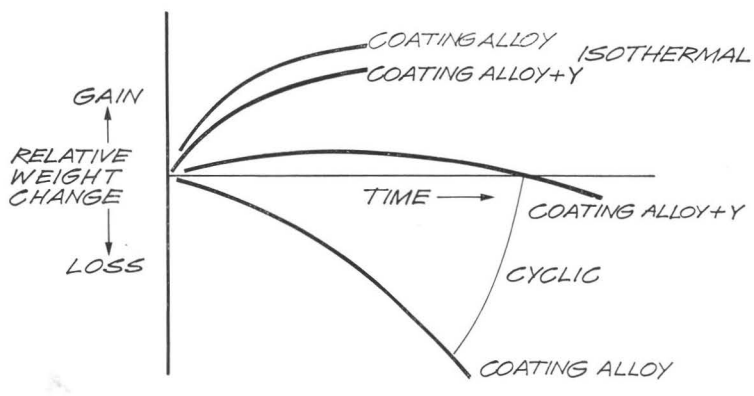

FIG. 10. — *Isothermal and cyclic oxidation behaviour of coating alloys with and without yttrium additions.*

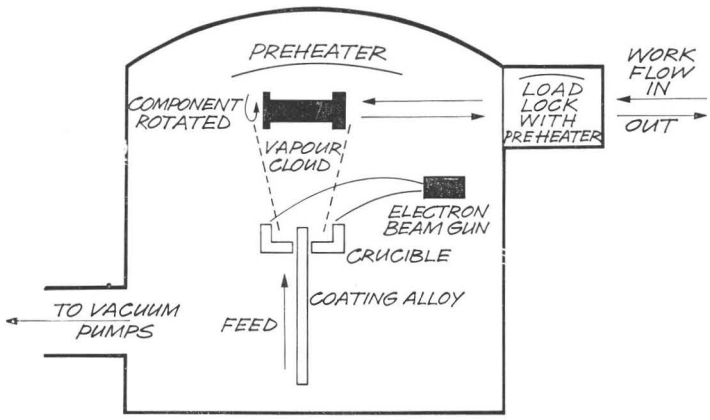

FIG. 11. — *Diagramatic representation of the vacuum evaporation of coatings.*

In this process the coating alloy is evaporated in a hard vacuum by an electron beam heat source. The preheated component is inserted into the vapour cloud created and rotated to expose all the surfaces to be coated to the vapour. After a suitable period the component is withdrawn and cooled in an inert gas filled load lock. Post coating operations include peening and a high temperature heat treatment to cause diffusion to occur across the interface and ensure a good structure and metallurgical bond. An example of a typical overlay coating is shown in figure 12. A disadvantage of this process is that the grain structure produced in the deposit can be columnar in nature if the processing parameters are not optimised.

In a variation of this process, ion plating, a potential is applied to the substrate and evaporation takes place in a glow discharge in the chamber with a soft vacuum 5×10^{-2} torr. The advantages are that a proportion of the metal vapour is ionised and attracted to the substrate, the impaction into the substrate improves the bond strength and the gas scattering imposed by the soft vacuum improves the coating uniformity. Columnar growth can also be avoided using this technique.

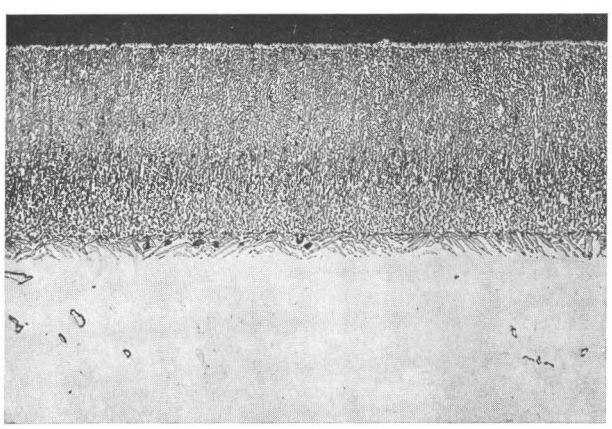

FIG. 12. — *Section through a typical overlay coating showing optimised grain structure.*

Earlier in the text mention was made of the importance of cost effectiveness, the physical vacuum evaporation process is an example of a technique which produces excellent coating but at a very high cost and this aspect more than any other is preventing its widespread use. The pressure is on therefore to develop a viable less costly alternative.

Among the other techniques being studied are the isostatic compaction of powder deposits applied by slurry or electrophoresis and the bonding of thin foils but the process most likely to compete economically and technically with the P. V. D. process is plasma spraying.

PLASMA DEPOSITION

In the past 5 years there has been a steady improvement in plasma gun technology with increasing particle exit velocities and the ability to apply deposits in an inert atmosphere. The technology is now available for the deposition of dense oxide free coatings but the production scale feasibility has yet to be demonstrated.

AREAS IN WHICH RESEARCH IS REQUIRED

1. The development of a new overlay coating process capable of producing quality coatings at low cost.
2. The development of a suitable coating process for the coating of internal cooling passages.
3. The development of a range of coating alloys each optimised to combat a particular environment.
4. Examine the properties required to combat high velocity particle erosion at typical turbine temperatures and identify suitable surface layers compatible with the overlay alloys.
5. The examination of surface loss mechanisms in cyclic oxidation and hot corrosion.
6. The determination of mechanical properties-Creep, L. C. F. and H. C. F. and interaction in typical turbine atmospheres.

It is important that any corrosion tests carried out to support coating development should be with burner rigs simulating as closely as possible true turbine condition *i. e.* with appropriate pressure velocity and fuels.

Rev. int. Htes Temp. et Réfract., 1977, t. *14*, pp. 28-45

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METALS AND ALLOYS FOR HIGH TEMPERATURE APPLICATIONS CURRENT STATUS AND FUTURE PROSPECTS

By

C. D. DESFORGES

INTRODUCTION

The task which has been given to me viz. a review of metals and alloys for high temperature applications is of such magnitude, both in the breadth of the topic and in the depth which is required to treat each constituent element of the spectrum of materials, that a few qualifying statements are necessary so that the limits of this paper can be clearly defined. Most of the papers presented at the Petten colloquium have been concerned with the specific requirements of a number of industrial sectors, both established and developing, which are of current prime importance in advanced industrial societies and will undoubtedly become important in the so-called emerging nations. I propose to identify the major alloy types which are in current use and to describe some of the basic principles which are believed to underly their properties and hence their applications. In particular I will describe recent developments in processing of these materials since control of manufacturing routes is leading to improved properties, cheaper products and greater quality control, which is so vital for components whose failure can have catastrophic consequences. An indication of problem areas and areas which merit further attention will also form a part of this paper.

1. PROPERTY REQUIREMENTS FOR HIGH TEMPERATURE APPLICATIONS

The large number of relevant properties, which are required in a high temperature material, deserve attention before describing the competitive metals and alloys of interest. If the refractory metals are included with the superalloys then service temperatures of 2,000° C can be considered as attainable. They must have creep resistance; fatigue resistance; thermal-shock resistance; good fracture properties and for b. c. c. metals, with a ductile to brittle transition, this temperature should be as low as possible; oxidation and hot-corrosion resistance; high stress to rupture values; ease of fabrication and joining; impact and erosion resistance; thermal properties, etc. By virtue of the wide range of engineering applications which require such materials, they must be available in a wide variety of forms: bar; castings, often of great intricacy; extrusions; forgings; sheet; tubings, and thus have to be processed economically by a number of production routes. Finally techniques are required so that the quality of the materials can be assessed and assured; their in-service behaviour has to be monitored and if at all possible this should be predictable from basic property data. This latter point is of some importance since materials are usually developed for service and our knowledge of their behaviour in operational service is significantly less than that of their « for service » properties, mainly as a result of the complex conditions in which a component functions at high temperature.

The large number of property requirements underlies the existence of materials problems, which are all the more difficult to solve when a combination of these factors is present. It is also worth considering how high temperature requirements can be met without having recourse to any specific material, since much of the existing technology of high temperatures makes use of such techniques to a greater or lesser degree. A component can be cooled either by a fluid or a gas, with a prime example being found in gas-turbine engines where blade cooling enables them to be used in gas temperatures exceeding those of the alloy melting

point. Insulation can be used to limit the effect of high temperatures, as can physical phenomena such as ablation, radiation, etc., typically employed in rocket powered space vehicles. The drawbacks to these various approaches are numerous *e. g.* weight tends to be excessive and hence power/weight ratio decreases; very complex cooling passages are required in turbine blades and this demands very complex technical solutions; reliance on ablation is obviously limited by a time factor since the material wears away and has to be replaced.

Materials thus offer the major solution to these problems and provide the only answer when long term reliability is necessary *e. g.* electrical power generation equipment. Two classes of metallic materials can be identified for high temperature applications viz. superalloys and refractory alloys based on chromium, tantalum, niobium, molybdenum and tungsten. Their relative merits and demerits can be summarised in terms of their high temperature strength (fig. 1); their resistance to atmospheric attack at temperature; their ability to withstand shock loading *i. e.* their fracture properties. Processing routes for the fabrication of components from these materials must take into account these three factors and furthermore they must be designed so that these desirable properties are improved by the processing operation. Developments in this area have led to significant advances in the last ten years and a major theme of this paper will be a presentation and critique of liquid-phase and solid-phase processing routes which are being developed.

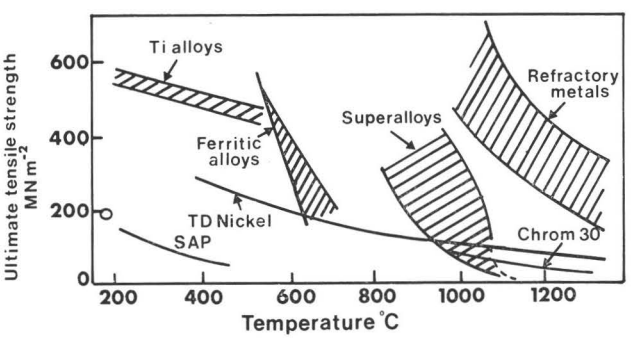

FIG. 1. — *Strength of high temperature alloys.*

Before discussing processing developments it is worth reviewing, albeit briefly, the salient features of superalloys and refractory alloys. Other papers at this colloquium have dealt in depth with specific properties and applications and there are several excellent publications to which reference can be made for more detailed information. What has to be borne in mind is the rapid pace of development of these materials and some sense of historical perspective is essential if the wide variety of developments are to be placed properly in context.

2. SUPERALLOYS

The name superalloys is widely used by metallurgists and engineers to cover a group of metallic alloys which have been developed, and indeed are now specifically designed, to function at high temperatures. More formally a superalloy is an alloy developed for elevated temperature service, usually based on group VIIIA elements (iron, cobalt and nickel) where relatively severe mechanical stressing is encountered and where high surface stability is frequently required.

Although there are only three basic types of superalloy based on the above definition, the technical and engineering literature abounds with a variety of materials, which have been developed for high temperature service. At the time of writing there are more than 100 superalloys commercially available and this quantity alone is a prospect which might daunt the most enthusiastic of designers concerned with the rational selection of the best alloy. An analysis of these alloys reveals complex compositions, forming methods from casting to forging, from controlled solidification procedures to powder metallurgy consolidation techniques using high pressures and temperatures.

The major driving force behind the development of superalloys has been the demand for more efficient power generation units, particularly gas turbine engines for military and civil applications in aerospace, marine and land based vehicles. The environment of a gas turbine component is one of the most demanding and aggressive situations which engineers have managed to devise and the ingenuity of the materials specialist has been taxed to the limit in attempting to satisfy these demands. It is not always appreciated that nickel and cobalt-base alloys have demonstrable useful strength at the highest fraction of the alloy melting point of any other alloy-systems, and if full use is to be made of this fact it is important that the basic factors controlling the properties of superalloys should be understood, even though at first sight they seem rather abstruse and complex.

This complexity stems from the interaction of several factors at high temperature and the difficulty of forming a strong solid to a precise form. Typical properties which have to be evaluated include strength, ductility, weldability, surface stability, formability, etc. The separate determination of each of these property groups has then to be followed up by an assessment of their relative change under the influence of changes in other parameters *e. g.* the effect of a heat affected weld zone on toughness. By defining what properties are of importance at high temperature the designer can then assess, albeit approximately, what emphasis has to be placed on chemical, physical or mechanical properties.

2.1. Property requirements and applications

It has been suggested that there are three types of property with which an engineer has to concern himself: quantifiable parameters, such as the stress rupture value at a given temperature; desirable but difficult to measure properties such as weldability and oxidation resistance; finally the desirable but unquantifiable properties, which include the rather unusual sounding term of « the forgiveness » of a material *i. e.* that the component will still function adequately even if fabrication errors have occurred. These three categories represent in order the decreasing ability of the designer to lay down

specifications for a given component. Stress typifies a property which can be exactly prescribed and measured.

The design is usually arranged so that there is a uniformity of stress *e. g.* by altering geometry or operating conditions. As soon as stress levels vary or fluctuate the problem becomes more complicated and the onset of fatigue failure cannot be predicted with any great degree of certainty. Since fatigue is clearly related to surface damage it must be recognised that most of the lifetime of a component is spent in the crack propagation stage. The interaction of creep phenomena with fatigue crack propagation complicates still further the total stress situation, and since microstructural changes are occurring the problem becomes difficult to solve on the basis of present knowledge of materials behaviour. Although stress is a readily calculated parameter, there will inevitably be a scatter of values, related both to testing error and also to a lack of chemical homogeneity in any given component. Segregation produced during solidification leads to different parts of a nominally overall uniform composition ingot having variations in property. This is obviously increased as component size increases and the difficulties are compounded since a decision has to be made on the degree of scatter in properties which can be tolerated. High temperature situations are demanding because failure can bring about dramatic structural collapse and little imagination is required to foresee the result of such failure in for example, aircraft engines. Hence safety margins must be high, reliability is all important and inspection techniques both rigorous and comprehensive have to be employed. Weibull analysis a most useful design tool, which has been used for brittle materials, can play a role in solving this problem.

Properties such as weldability, surface stability, machinability are clearly important for high temperature materials but the establishment of absolute values has not been possible. Ranking schemes are usually adopted and relative comparisons made so that the suitability of two competitive materials can be measured. Interactions of such properties can lead to situations where no obvious solution can be found short of a decision based on experience, since a balance is being struck between parameters which themselves cannot be quantified. *e. g.* oxidation resistance, as has been clearly shown in a previous paper at this conference by Dr. Whittle. High temperature exposure usually leads to two, well recognised phenomena: the alloy surface is degraded because of reaction between the solid and the gaseous environment, which itself is a consequence of the innate tendency of the alloy to revert to a lower energy state *e. g.* oxide, sulphide, etc.; the alloy undergoes permanent plastic deformation under a constant stress, the amount of deformation being a function of time *i. e.* it is said to creep. The resistance of an alloy to both these factors basically determines its ability to function adequately at high temperature. Corrosion or oxidation resistance is vital since the gaseous surroundings of many high temperature components often contain sulphur, chlorine, sodium, which, even though present in small quantities, have profound effects on the surface stability of the alloy. Since this form of attack consumes metallic constituents, it is important that the component retains adequate load-bearing properties in the reduced section thickness. Clearly, if a thin-walled tube is subjected to hot corrosion, the possibility exists that it can be perforated and design specifications must ensure that materials of high corrosion resistance are used in critical areas. Unfortunately this problem is complicated by three factors: the difficulty of translating laboratory measurements to full scale structures; the difficulty of simulating industrial conditions so that true performance data can be obtained; the large number of variables present in a high temperature corrosion reaction, which makes exact life prediction from simple data an almost impossible task.

Creep phenomena also present a considerable challenge since most of the empirical data obtained by testing cannot be used to predict eventual component life with any degree of exactitude. Until a direct reading indication of the exact state of a component with respect to its overall life is developed, great caution is required in extrapolating test results to longer times, higher temperatures or higher stress levels. This is a very real problem for the designer since the desirable goal of longer life can lead to lower maintenance costs, greater use of plant, higher availability, etc. But how can this be ensured in practice unless a test equal in duration to that of the expected service life is carried out ? No clear answer is available, although there are some indications that work at the National Physical Laboratory (England) to obtain microscopic information on the creep state of an alloy in service, is showing significant promise. The interplay of surface stability and creep resistance leads to the necessity for subjective value judgements, since it is almost inevitable that an improvement in one leads to a deterioration in the other. An excellent illustration of this can be found in the well known fact that, although chromium additions to steel improve oxidation resistance (through forming a protective oxide layer) the creep resistance decreases significantly, in some cases by an order of magnitude.

Having established a simple framework of properties which are essential for satisfactory high temperature service, the ways in which superalloys have been developed to satisfy these demands will be described in detail. An understanding of their basic metallurgy is essential if full advantage of these alloys is to be taken. They represent a significant technical achievement starting from the days of Whittle and the first jet engine to advanced engines powering *jumbo jets*, marine propulsion units, gas and oil pumping units, etc.

As an indication of the economic advantage which can be gained from running power plant at higher and higher temperatures, it should be pointed out that an increase from 900º C to 1,050º C in the inlet temperature of a gas-turbine engine increases the specific thrust by 10 %. If the temperature can reach 1,250º C then the increase is 30 %. Two approaches to this problem have been used: one has relied on the development of alloys with increasingly refractory properties; the other, an engineering design solution, has relied on the use of convection cooling of the components. In reality a combination of both is used, but the demands placed on materials are such that they are used in gas tempe-

ratures which are very close to the alloy melting point. The development of new alloys to satisfy these stringent requirements is a remarkable testament to the application of physical metallurgy principles to practical problems. Early gas-turbine engines contained only 10 % by weight of superalloys and operated at temperatures up to 815º C. The latest U. S. engines now contain up to 70 % by weight although UK engines contain significantly lower quantities of superalloy. Since aero-engine technology tends to run well ahead of industrial engine developments, it can be expected that the spectacular improvement in aero engine performance (halving specific fuel consumption; tripling specific thrust values; improving between-service life from 100 hours to 1,200 hours) will eventually be realised in land based units. The importance of energy conservation is receiving increasing attention and one obvious way of achieving this very desirable aim is to make the conversion of fuel oil to electrical power more efficient. In principle there is no reason why aero-engine efficiences of 55 % to 60 % cannot be achieved in industrial engines, in comparison with maximum, present day, levels of 40 %. The problems in many ways are less severe for a land-based unit since power to weight ratios are not as critical as for an aero engine. Furthermore there is far less thermal cycling in a power generating unit and hence thermal fatigue is almost eliminated. Oxidation difficulties are also reduced because thermally induced spalling of the protective oxide layers or of coatings is avoided. By using the superalloys, significant economies should prove possible in industries such as electrical power generation, land-based transport systems (rail and road); gas and oil pumping.

2.2. **Physical Metallurgy background of Superalloys**

Superalloys are based on the existence of stable, face centred cubic phases (austenite) based on iron, cobalt or nickel and their most useful property is the retention of very high strength levels at large values of the ratio-operating temperature/alloy melting point—known also as the homologous temperature. Equivalent body centred cubic alloys do not have this characteristic. This property is also accompanied by high modulus values and good diffusivity of secondary alloying elements in the austenitic lattice. A vital factor in the development and retention of elevated temperature, mechanical properties has been the solubility of other elements in the austenitic matrix and the consequent possibility of forming strong intermetallic compounds based on nickel-aluminium (γ'), which are stable to relatively high temperatures.

The various elements present in these superalloys are specifically added to satisfy some service requirement and alloy development has been a series of compositional modifications designed to improve specific properties without adversely affecting the other. Table I shows in schematic form the role played by the various elements and indicates the complexity of the nickel-base alloys, whilst table II is a similar categorisation for cobalt-base alloys.

A schematic resume of the temperature ranges in which these various mechanisms operate and their effect on tensile strength and ductility values is shown in figure 2. Although this representation is not comprehensive in that dispersion effects both of strong fibres and stable particles have been left out, it gives a clear picture of the problems which new materials are called upon to solve.

Superalloys can be regarded as being a logical development step from stainless steels, which contain sufficient chromium to form a protective oxide layer upon exposure to high temperature. As an intermediate step there is a generic family of nickel-iron superalloys based on the formation of a stable austenitic phase through adding at least 25 % of nickel to the iron. The nickel not only stabilises the austenite but also promotes the formation of intermetallic phases containing either titanium or niobium. In this way the iron base superalloys can be used to higher temperatures (with a potential of about 800º C/825º C compared to 1,150º C for nickel base superalloys) possessing good stability but relatively poor oxidation resistance (although recent developments [1, 2] have indicated that iron-base alloys with excellent oxidation resistance properties can be produced for certain aerospace and gas-turbine applications). As a general rule the cost increases with increasing nickel content and certain components destined for high temperature service can be made from

TABLE I. — *Role of elements in nickel-base superalloys.*

Effect	Element						
	Co	Fe	Cr	Mo, W	V Nb, Ta, Ti	Al	C, B, Zr
Solid Solution strengthening. . .	X	X	X	X	X	X	
Intermetallic compounds formation.					X	X	
Grain boundary segregation. . .							X
Carbide formation.			X	X	X		X
Protective oxide formation. . .			X			X	
Typical alloys							
Nimonic 263	20	0.75	20	5.9--	--2.15	0.45	0.06 0.001 0.02
IN 100.	15	—	10	3.0-1.0	--4.7	5.5	0.18 0.014 0.06
Hastelloy X	1.5	18.5	21.8	9.0 0.6-	---	—	0.10- -
Rene 41.	11	5.0	19.0	10--	--3.1	1.5	0.09 0.002 -

TABLE II. — *Role of elements in cobalt-base superalloys.*

Effect	Ni	Cr	W	Ti, Zr, Nb, Ta	C
Solid Solution strengthening. .	X	X	X		
Intermetallic compound formation		X	X		
Carbide formation.		X		X	X
Protective oxide formation. .		X			
Typical alloys.					
X 40.	10	25	7.5	—	0.45
L 605	10	20	15	—	0.10
HS 188	22	22	14	—	0.08

a low nickel content, iron base superalloy rather than the more expensive nickel base alloys. As well as being cleaper the high content iron alloy systems are more deformable and have high melting points and better machinability than the nickel-rich alloys. A particular drawback of the iron-base superalloys is their tendency to form embrittling phases both as a result of transformation of the strengthening Ni_3 (Al, Ti) and Ni_3Nb and also directly from the matrix *e. g.* Laves phases. Although increasing the application temperature will tend to rule out the wider use of iron-base alloys, they are still by far the largest volume of superalloy in service at temperature up to 800º C. One method of improving their properties at intermediate temperatures would be to develop a cheap precipitation process *e. g.* by adding manganese instead of nickel, and hence retaining the cost advantage of the iron-base alloy.

Applications, which could utilise such alloys, include small gas-turbine engines for land based transport units

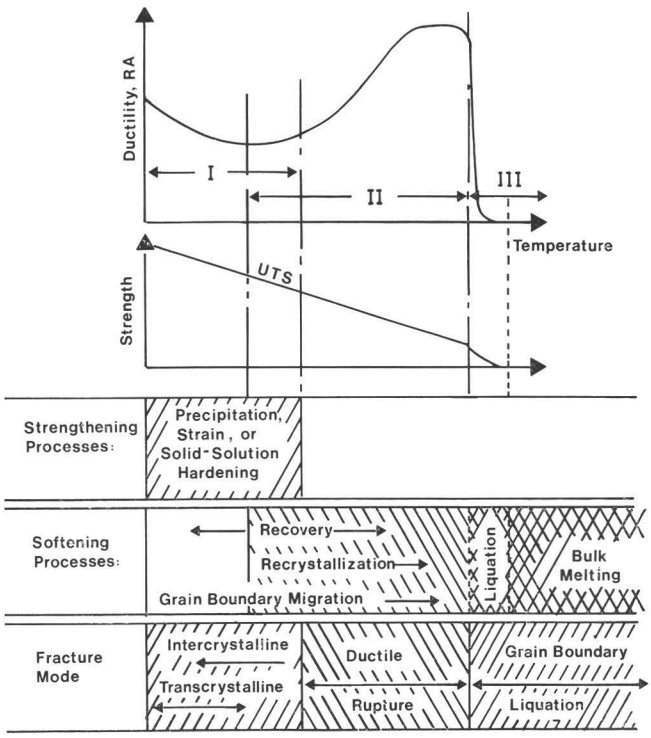

FIG. 2. — *Schematic portrayal of hot strength and ductility factors* (*Courtesy* of Welding Research Society).

e. g. lorries, buses and possibly automobiles. Powder metallurgy processing routes, which will be discussed later, may also lead to the use of iron base superalloys at much higher temperatures provided that the problem of a lack of tensile strength at intermediate temperatures (600º C to 750º C) can be overcome. This possibility exists because control and variation of the alloy composition will be greater using powders as a starting material in a processing route which uses consolidation by pressure.

2.2.1. **Strengthening mechanisms.** — The limitations outlined above are to a large extent overcome by both cobalt and nickel-base alloys, although each alloy group has specific advantages which allow them to be specified for a wide range of high temperature applications *e. g.* energy generation (gas turbines; jet engines; steam turbines; nuclear reactors); transportation systems (land, sea and air propulsion units); petrochemical plant. The largest potential is in gas-turbine engines and the desire to generate and use energy more efficiently will certainly lead to increasing usage despite their high cost. The state of-the-art position of alloy chemistry and alloying processing will now be discussed in detail before briefly reviewing some of the likely developents in superalloy technology. The major strengthening effect is achieved by adding to the austenitic matrix elements which, although they are totally soluble, distort the crystal lattice, so that dislocation motion, which is the prime cause of plastic flow in metals, is prevented. This effect is produced by additions of tungsten, molybdenum, tantalum, etc., although their efficiency is somewhat diminished by their high densities (table III). Cobalt and chromium, although added for other more important reasons, also increase the basic strength of the nickel matrix (as do nickel and chromium in a cobalt matrix). Improvements in mechanical strength at temperature of various grades of nickel-base superalloy have been obtained by increasing the amounts of alloying element as is shown in table IV.

The development of strength by the formation of a stable ordered, coherent intermetallic compound $Ni_3Al(\gamma')$ is of great importance in retaining strength at intermediate temperatures (about 750º C) in nickel-base superalloys. In general about 30 % by volume is formed during heat-treatment. In contrast cobalt-base super-

TABLE III. — *Elements present in superalloys.*

Metal	Melting Point (ºC)	Density Kg $m^{-3} \times 10^3$
Iron	1,536	7.85
Nickel . . .	1,455	8.9
Cobalt . . .	1,492	8.71
Chromium . .	1,850	7.2
Niobium . . .	2,468	8.55
Molybdenum. .	2,610	10.2
Tungsten . . .	3,410	19.3
Tantalum . .	2,996	16.6
Aluminium . .	660	2.70
Titanium . . .	1,668	4.5
Carbon . . .	3,730	2.25

TABLE IV. — *Development of nickel base alloys.*

Alloy Type	Composition (wt%)						Property
	C	Cr	Co	Mo	Al	Ti	100hr stress rupture at 850° C MNm^{-2}
Nimonic 75	0.12	20	—	—	—	0.5	112
80A	0.08	20	—	—	1.5	2.4	130
90	0.10	20	17.5	—	1.6	2.4	172
95	0.12	20	17.5	—	2.0	3.0	228
100	0.20	11	20	5	5.0	1.3	239
105	0.15	15	20	5	4.7	1.2	285
115	0.15	15	15	3.5	5.0	4.0	320

alloys cannot be strengthened in this way because the precipitates dissolve at relatively low temperatures (about 800°/850° C) and they also possess an undesirable morphology. Research efforts to develop an equivalent cobalt-tantalum or cobalt-titanium compound are continuing and it is quite possible that in the future such phases will be produced in commercially available systems.

The properties of Ni_3Al are quite unique in that its strength increases with increasing temperature and it also possesses inherent ductility, unlike other strengthening phases such as carbides and borides, and in direct contrast to the severe loss in ductility which occurs when other intermetallic compounds *e. g.* sigma and Laves, form after heat-treatment or prolonged high temperature exposure.

The strengthening mechanism of γ' particles is now reasonably well understood. When the volume fraction is high and particles are fine in size, the particles are essentially stringed together and can be looked upon as a continuous array so that dislocation cutting of particles can occur. For the case of high strength nickel-base superalloys with a high volume fraction of γ' particles the strengthening theory of Copley and Kear [3] can be applied to explain their strength/temperature properties.

Regardless of γ' morphology, the yield strength of nickel-base superalloy drops fairly abruptly at about 760° C. This finding is consistent with a decrease in the degree of ordering in the γ' particles and an associated sharp decrease in Antiphase Boundary (APB) Energy which is the dominant restraining force to dislocation motion during yielding. Above 760° C the position of the strength-temperature change depends on strain rate, with the change moving to higher temperatures as strain rate is increased. This strain rate dependence strongly indicates that the disordering process in γ' is caused by the intruding dislocation and involves a kinetic process. The strength drop-off in nickel-base superalloys is a consequence of disordering about γ' by vacancy diffusion and a lowering of the APB. The suppression of such a diffusion process is impossible to accomplish by changes in γ' morphology or by processing means. Changes in γ' morphology will not affect the location of the strength drop and it is not affected by processing as results on thermomechanical treatments [4] and controlled solidification [5] of nickel-base superalloys have shown. In addition, recent results have confirmed that the strength loss- temperature of the current high strength nickel-base superalloys is about as high as one can achieve through alloying means.

Grain boundaries have always been the weak links in nickel-base superalloys and whilst they are strengthened by precipitates *e. g.* intermetallic compounds, carbides, or by elements *e. g.* boron, zirconium, hafnium, the strengthening effects will tend to be reduced during elevated temperature applications under load. This results from stress induced diffusion between grain boundaries where chemical changes can occur, resulting in the dissolution of strengthening phases at certain grain boundaries and a consequent deleterious loss in strength. By using coherent particles to strengthen a single crystal alloy it may be possible to avoid this adverse effect, but a gradual degradation of strength properties is inevitable in polycrystalline alloys operating at high temperatures under load. This means that the application of polycrystalline nickel-base superalloys is restricted to those temperatures where stress-induced diffusion is strictly limited [6]. Diffusion is thus the limiting factor controlling both the intergranular strength-loss temperature and also intergranular phase instability. This also suggests that improvements in mechanical properties will be obtained if phases that are immune to diffusion effects *e. g.* insoluble oxides, can be added to γ'-containing alloys. The first exploitation of this effect was in the production of ThO_2 dispersoids in nickel with the resultant alloy being known as T. D. Nickel [7] and its most recent success has been the use of high energy, dry, agitation milling of metallic powders with oxides in attritors [8] to produce a new type of superalloy. This process has been colloquially termed mechanical alloying [9] because of the intimate and homogeneous degree of mixing which is obtained by the milling action. This will be discussed later in this paper.

In addition to intermetallic compound strengthening, there is a further beneficial effect on creep resistance resulting from carbide formation in the grain boundaries. Cobalt-base superalloys depend on the formation of carbides for a large proportion of their strength, since intermetallic compound formation leads to severe embrittlement problems, and hence relatively high carbon contents (up to 1 %) are found compared to nickel superalloys (up to 0.2 %). The carbides tend also to form in the cobalt matrix rather than in the grain boundaries as is the case with nickel base superalloys.

The role of carbides is both complex and controversial, since opinion is divided as to whether or not nickel alloys should contain grain boundary carbides. Carbon free alloys show markedly lower creep life and it is now agreed that about 0.03 % to 0.05 % carbon is necessary for adequate rupture strength at high temperatures. The relative stability of the various carbides (from MC to M_6C where M is the metal) is a controlling factor in the long-term degeneration of superalloys at high temperatures. The most stable carbide (TiMo)C is a source of carbon for the formation of other carbides, particularly above 980° C, and it has been shown that for very long times (greater than 5,000 hours) the carbon content can decrease to such an extent that MC phase is totally absent. The intermediate carbide $M_{23}C_6$ (based on $Cr_{21}(MoW)C_6$) has a significant effect on properties, possibly by preventing grain boundary sliding and hence increasing rupture strength.

The cobalt alloys are strengthened to a large degree by MC carbides (Ta, Ti, Nb, Zr). These also furnish carbon for the formation of $M_{23}C_6$ phases which, if present as a fine dispersion, can act as a further strengthening phase.

2.2.2. **Thermal effects.** — With such a wide variety of potential secondary phases in superalloys the influence of heat-treatment has to be considered in terms of optimising the microstructure; the effect of joining procedures; the long term degradation of the phases during service. Since there are many elements present, the first step is to solution treat the alloy to ensure that a homogeneous solid is formed, free from any segregation present as a consequence of casting. An aging treatment is then carried out at temperatures in the range 750° C to 850° C so as to form γ' and carbides. The amount of γ' which forms is a function of the relative amounts of aluminium and titanium and, as table IV shows for a simple alloy system based on nickel-chromium, the rupture strength is increased by almost a factor of three when aluminium and titanium are added. The presence of iron and cobalt will increase the amount of γ' formed at any given level of titanium and aluminium. The carbides are usually precipitated at grain boundaries during heat-treatment and care has to be taken to ensure that they do not form as a continuous film, since such a morphology will lead to brittleness at ambient temperatures. Optimum mechanical properties are obtained when a uniformly hardened matrix is accompanied by a fine dispersion of carbides in the grain boundary. The complex nature of the possible reactions in superalloys can also lead to grain size increases for both wrought and cast alloys. It should be recognised however that there is a limit to the fineness of the grains in that creep deformation tends to increase for grain diameters of about 1μm. As will be described later, practical use can be made of this relative ease of deformation of ultra-fine grained alloys so that a very strong material can be superplastically formed at very low loads. Creep deformation occurs in crystalline solids by three processes: grain boundary sliding, Herring-Nabarro or Coble diffusional creep, dislocation creep. If grain boundaries could be completely eliminated then the first two processes would be inoperative and creep resistance markedly improved. By controlling the directional solidification of an alloy so that grain boundaries are reduced or even eliminated, a practical application of this idea has been developed in the last ten years [10].

The presence of boron and zirconium in very small amounts has been found to be essential if high temperature creep resistance is to be obtained, although the exact mechanism, by which this improvement is brought about, is far from being understood. Since creep is essentially a diffusion controlled process, these elements may well interact with vacancies in the grain boundaries and reduce diffusion rates hence increasing creep resistance. A very recent development, which has markedly improved cast nickel-base alloys, has been the discovery that hafnium additions (up to 1.5 %) significantly improve ductility by modifying the carbide morphology.

Since superalloys have to withstand heavy loads for long times at elevated temperatures, components made from them have to be designed so that microstructural changes occurring during operation, which may result in a reduction in property levels, can be taken into account or minimised. Typical of these effects are an increase in precipitate size and a consequent reduction in strength, and also the formation of an embrittling phase (known as sigma) which causes very low ductility at room temperature. Similarly the grain size, which influences both tensile strength and creep strength, can alter with time at high temperatures, particularly when the initial grain size is not uniform throughout the component. Superalloys, which have been forged to final shape, will generally have a more uniform grain size than a cast alloy and at service temperatures lower than 0.5 Tm (where Tm = alloy melting point) forged alloys may prove to be superior to cast alloys. However above 0.5 Tm the as-cast alloys have superior creep properties, although this behaviour is usually attributed to the very high levels of hardening elements, which can be obtained in cast alloys, rather than to a grain size effect.

As mentioned earlier advantage can be taken of the fact that a component, which has most if not all of its grain boundaries parallel to the axis of stressing, will have improved ductility and thermal fatigue resistance plus greater rupture strengths, when compared to the identical alloy which has a random distribution of grain boundaries. The use of directional solidification to achieve this grain morphology will be discussed later when the influence of new processing technology on the properties of superalloys is described.

Cobalt-base alloys are distinguished from nickel-base alloys in several ways. They differ microstructurally because of the absence of hardening phase of γ' type, and they differ in composition having fewer alloying element additions. This latter point leads to little if any heat-treatment procedures being carried out on cobalt alloys, the carbide phases being formed during solidification. Only if recrystallisation or stress-relief are required are wrought alloys heat-treated, whilst cast alloys are sometimes given solution treatment followed by aging to reprecipitate carbides in a finer form, so that rupture strengths are increased. Although cobalt alloys have adequate ductility values at room temperatures especially after long term exposure to high temperatures.

As a consequence of microstructural differences the mechanical properties of nickel and cobalt superalloys vary as a function of temperature and the detailed manner in which this variation occurs dictates the applications which they can fulfill. In general the nickel base alloys have far superior tensile strengths up to 750° C; above this they tend to be of the same order of magnitude since the γ' phase becomes of less importance as it grows and eventually dissolves at high enough temperatures. At temperatures in the range 1,000° C to 1,200° C solid solution strengthening is the only source of mechanical resistance in conventional superalloys and hence nickel and cobalt alloys tend to be controlled more by their melting points with respect to the operating temperature. When rupture strength is considered the major difference depends on the lower rate at which

it decreases with cobalt superalloys than for nickel superalloys. Thus at low temperatures the nickel base alloys are more resistant but this advantage is lost above 900º C, and cobalt alloys become competitive on strength grounds alone. As a further consequence of the relatively simple chemical compositions of cobalt alloys, higher melting points are measured than for nickel alloys so that at equal operating temperatures cobalt alloys are operating at lower ratios of service temperature to melting point than are the nickel-base alloys.

An important difference between nickel and cobalt superalloys is related to the superior hot corrosion resistance claimed for cobalt-base alloys in atmospheres containing sulphates, sodium salts, halides, vanadium and lead oxides, all of which can be found in fuel burning systems. Nickel forms a low melting point eutectic with nickel sulphide and hence in sulphur-bearing gases attack of the alloy surface is rapid and drastic. In contrast it is commonly believed that the oxidation resistance of nickel alloys is superior to that of cobalt based systems, because the relatively high aluminium contents of nickel alloys promote the formation of surface films of Al_2O_3 during oxidation in air, whereas the cobalt alloys rely on Cr_2O_3 formation for their high temperature oxidation resistance (in general Al_2O_3 films are more protective than Cr_2O_3 layers). The difficulty in selecting an alloy for high temperature service is compounded by the problem of relating laboratory data obtained by oxidation testing to in-service performance. For protection to be of any value the oxide layers must be adherent and in particular they have to remain adherent during thermal cycling (from high operational temperatures to ambient and *vice versa*). Loss of the oxide by spalling exposes a metallic surface which will then be oxidised in turn, thus consuming metal. This loss of metal can be critical for thin sheet material since perforation may well occur with catastrophic consequences for components such as combustion chambers, cracking chambers, etc. Even if perforation does not occur, oxidation will tend to reduce the load bearing capacity of a component since the metal cross section is reduced. A phenomenon of some consequence to designers is the penetration of the metallic alloy phase by oxides down grain boundaries. This is known as internal oxidation and assessment of this tendency is just as important as knowledge of the overall weight change resulting from oxidation. Recent developments in cobalt-base superalloys have tended to increase oxidation resistance by adding aluminium and silicon, whilst the addition of rare earth elements such as lanthanum [13] and cerium [14], and also yttrium [15] in very small quantities (less than 0.1 %) has been shown to give very marked improvements in the cyclic oxidation resistance of both cobalt and nickel-base alloys. Despite these improvements it has been found necessary to supplement their oxidation and corrosion resistant properties by the use of coatings which usually contain aluminium and chromium and act both as a protector of the alloy surface and also as a barrier to oxygen and other elements present in the atmosphere in which a given component has to operate. The limiting factor for the use of all superalloys is likely to prove to be their chemical resistance (both oxidation and hot-corrosion) since it has now been shown that adequate mechanical strength can be obtained by adding inert phases, which remain stable up to the melting point of the metallic matrix. Coating technology, no matter how effective it now is or will be in the future, will not allow superalloys to be above 1,200º C for very long times.

The next step must be to use the refractory metals (niobium, tantalum, chromium, molybdenum, tungsten) or refractory, low density ceramic phases such as silicon carbide or nitride, with the distinct possibility that compounds based on silicon, aluminium, oxygen and nitrogen will become available through controlled reaction of powders with gaseous atmospheres. The attraction of the latter step lies in the wide abundance of cheap raw materials. Problems however will certainly arise because of the brittle behaviour of these compounds. The stress situation is simplified by virtue of the assumption that the component operates under elastic constraints. Surface defects or surface damage can markedly increase susceptibility to brittle failure, since these materials lack the ability to accomodate local stresses and strains from any number of sources. This will thus require very stringent analysis of the probability of failure and attempts will have to be made to reduce property scatter to a minimum so that Weibull techniques can be applied [17].

The importance of fatigue can be gauged from an estimate that about 90 % of engineering structures fail by fatigue [18]. Cyclic loads are difficult to predict in service and their effect on materials is dependent on microstructural characteristics and on macrostructural features, both of which are controlled by the processing route used to fabricate any given component. In contrast to low-temperature fatigue, which is characterised by transgranular initiation and propagation, high temperature fatigue usually results in intergranular fracture since slip-band cracking is suppressed as plastic deformation becomes more homogeneous and grain boundary sliding occurs. This problem is rendered more complex for high temperature materials, since there are the additional possibilities that thermal fatigue can occur as a result of non-uniform heating and cooling during thermal cycling and oxidation/hot corrosion phenomena will produce localised intergranular failure at the surface.

Nickel-base superalloys have relatively poor fatigue resistance, as can be seen from a comparison of their endurance ratio (endurance limit to yield strength) of approximately 0.25 with those of pure metals *e. g.* iron, nickel, aluminium with values of 1.0 and iron-base alloys with values varying from 0.5 to 1.0. Fortunately, because of the high yield strength of γ' and its maintenance at high temperatures, nickel base superalloys can still be used in fatigue. Casting defects can also be eliminated by a very novel process (H. I. P.) using a combination of high temperature and the simultaneous application of isostatic pressure [19]. The action is essentially a « healing » one and it is particularly effective for large, poor quality cast components of varying cross-sectional dimension with a consequent beneficial effect on fatigue properties.

Compositional control can also be used to improve fatigue properties. By lowering the carbon content so that the volume fraction of carbides is reduced a significant increase in the endurance ratio can be obtained. The production of a microstructure, which improves high temperature strength and maintains good ductility values, will materially assist situations as the low endurance ratio does not vary greatly with temperature.

Structural defects such as voids, casting porosity, cracked phases, massive heterogeneous grain boundary phases can all act as initiation sites for fatigue cracks. The importance of processing control so as to avoid or limit such defects has been realised and both directional solidification techniques and thermomechanical treatments can be used to achieve this objective. Gas porosity is significantly reduced both in size and density during directional solidification probably as a result of the absence of a dendritic microstructure which normally traps gas bubbles during solidification. Similarly a high degree of mechanical working can break up crack-nucleating brittle phases and close pores.

2.3. **Processing**

The processing of superalloys has tended to develop in terms of the choice of a certain alloy composition selected so as to provide specific mechanical or chemical properties *e. g.* a certain creep resistance or ability to withstand hot fuel gases without corroding significantly.

A useful framework within which processing developments can be described and classified, separates liquid phase technologies, involving primary melting and solidification in controlled atmospheres to produce specific microstructures in complex forms, from solid state processing, in which the ascast solid ingot is shaped by applying mechanical forces. Developments of specific processes occur for a variety of reasons and a complete discussion of them is beyond the scope of this paper. As an illustration of this point powder metallurgical technology has arisen in response to segregation problems which occur when a multiphase alloy solidifies. Each powder particle can be looked upon as being a micro-ingot and hence the scale of segregation is greatly reduced (almost to zero in some cases). Since the elimination of chemical heterogeneity is achieved by diffusion, a shortening of the diffusion path leads to shorter times to achieve homogeneity since the time is a power function of the distance. Powder metallurgical products are hence more homogeneous in composition compared with cast alloys and the flexibility of controlled compositional variations is greatly extended.

2.3.1. **Processing effects on purity.** — A primary melting and casting operation would ideally produce a clean, uniform chemical composition, impurity and gas-free solid having a specific microstructure characterised by its uniformity, with a high material utilisation factor (low scrap levels) using a reliable, readily controlled inexpensive process. Reality is obviously some way from this ideal condition, but two specific processes: a primary melting in vacuum using induction heating (VIM) [21] and a secondary vacuum remelting operation [22] using high current low voltage electric arcs between a molten metal and a consumable electrode of the required alloy (VAR) have been developed for, and are widely used in, the production of nickel base superalloys which have to be made to very close compositional limits. As a complement to vacuum arc remelting an air melting process known as electroslag (flux) remelting (EFR) has been developed [23]. It depends for its action on the use of a consumable electrode of the final alloy composition which is submerged in a molten, chemically active, flux resistance heated by an electric current passing between electrode and molten pool beneath the flux (fig. 3) [24]. As the electrode melts droplets of alloy form and they are refined on passing through the flux. The refining rate is rapid because the droplets have a high surface area/volume ratio, resulting in the removal of most of the impurities and a significant reduction in inclusion content. This improvement in alloy chemistry is reflected in superior hot-workability and in improved mechanical properties compared to vacuum arc processed material.

Other melting techniques using electron beams (EBM) and plasma arcs (PAR) as heating sources have also been developed, especially for alloys where very strict impurity limits have been specified; but it is still too early to predict the future development of these novel technologies. Table VI summarises the various possible effects of some of these melting and refining processes.

The superalloys can be processed directly to shape via a casting route *e. g.* « lost-wax » investment methods or by shaping the cast ingot through the use of mechanical force *e. g.* rolling, forging or extrusion, the choice depending amongst other factors on the shape of the final component. Early compositions of nickel-base

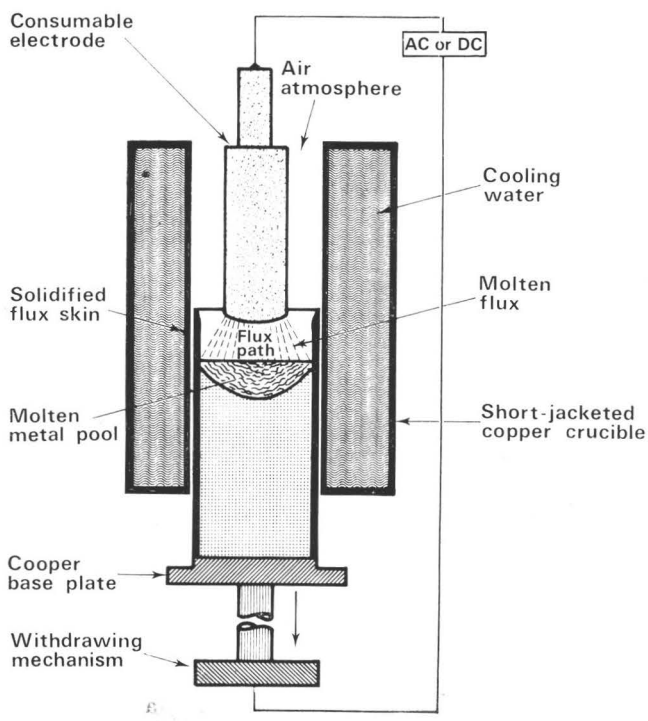

FIG. 3. — *Electroslag remelting using withdrawable ingot mechanism.*

alloys were developed so as to overcome the drawback of the relatively poor creep resistance of stainless steels, and the Nimonic series were all used in the forged condition mainly to make turbine blades and combustion chamber sheet. As strength requirements increased, alloy compositions were developed so as to satisfy this need, but the very fact that high temperature strength is produced leads inevitably to problems in hot working the alloy to shape. This difficulty can be overcome by using casting technology and hence producing very strong alloys, which can serve at higher temperatures than their forged counterparts. Processing developments have now taken over from compositional developments as the major route by which improved superalloys can be made and most of the present- day technology controls the properties of the final product through process variations, selected so as to give specific microstructures in complex shaped objects. This is an important point to recognise, since components such as turbine blades, etc. have their form controlled by engineering requirements *e. g.* aero-dynamic profile.

The pace of technical advance in the processing of superalloys can be measured in terms of a 1940 baseline when they were all without exception air melted, compared with 1976 when vacuum melting; electro-slag refining; directional solidification; superplastic forging; hot isostatic pressing of powders; dispersion strengthening are all in practical service as different parts of the overall processing route, whether it be through the liquid-solid transformation or solid-solid transformations.

The importance of these processing developments with respect to rupture strength is shown in figure 4 which demonstrates how the performance and temperature capability of gas-turbine blades have been improved in the last thirty-five years. The specific processes are detailed at the appropriate point on the graph.

Quality is greatly improved if impurities such as oxygen and nitrogen can be removed or at least minimised since they form inclusions which have a deleterious effect on mechanical properties such as fracture toughness. Vacuum melting and casting is able to achieve this result and spectacular increases in stress-rupture properties have been obtained in superalloys treated in this way, the effect being attributable to grain size and segregation control. Similarly investment casting, which had been carried out in air, is able to use the vacuum melted charge alloy and can also be performed in vacuum chambers (as the mould is easier to fill in the absence of air). Closely controlled compositions and lower metal pouring temperatures, grain size control to be achieved so that higher strength castings are possible. Recent developments in turbine technology have led to the use of internally cooled components and these intricate cooling passages can be made by using complex ceramic cores in an investment mould.

The production of these internal passages in high strength nickel-base alloys has been made possible by the application of electrochemical machining techniques. The external surfaces of components such as blades can be machined by conventional, well-established operations such as grinding and milling and also by electrochemical techniques. A complex air cooled blade can thus be made out of a solid blank although the cost

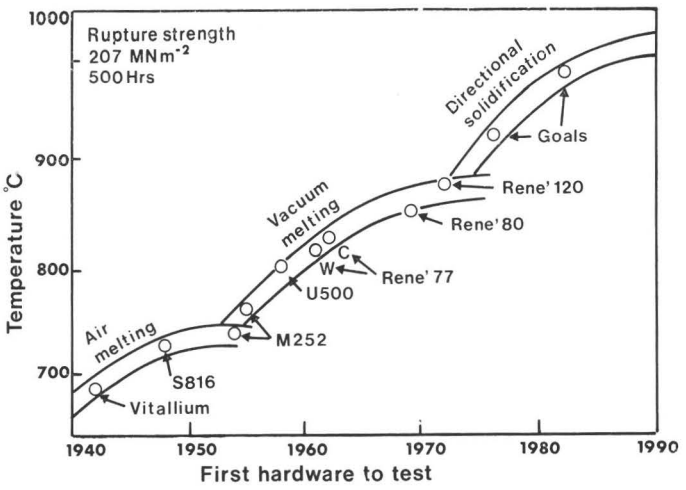

FIG. 4. — *Progress in turbine blade materials.*

of such an operation will be very high and the metal utilisation ratio will be very low leading to large amounts of discard material. The comparative rates of typical machining processes is shown in table V.

TABLE V

Machining Process	Superalloy Metal Removal Rate (in^3/min)
Grinding	12
Turning	3
Milling	3
Electrochemical machining	1
Electrical discharge machining	0.1

This represents a major advance since a higher operating temperature of the gas can be used without changing the alloy composition and the designer has been able to retain a material which has been fully characterised and with which he is thoroughly familiar.

2.3.2. **Processing effects on microstructure.** — An analysis of the mechanism, by which creep-rupture failure occurs, has revealed the importance of grain boundaries which are normal to the stress axis. By controlling the solidification process so that a steep temperature gradient is obtained and the solid/liquid interface moves in the direction of heat flow, these boundaries can be eliminated. This is now being exploited commercially for nickel base alloys (MAR-M200), with improvements in creep rupture strength at 982° C of about two orders of magnitude compared to a conventionally cast alloy (fig. 5). The ultimate limit of this technique is the production of a single crystal component which has no grain boundaries at all, and hence the elimination of grain boundary segregation. Practical exploitation of this has been demonstrated but the economic justification for the expense involved has not been fully established since there is a cost penalty of four times the conventional casting costs for uni-

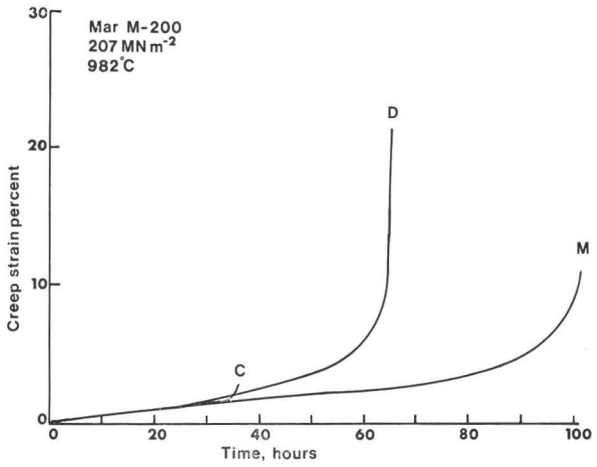

FIG. 5. — *Comparison of the creep properties at 982° C of conventional* (C), *directional* (D), *and monocrystal* (M) *mar-M200.*

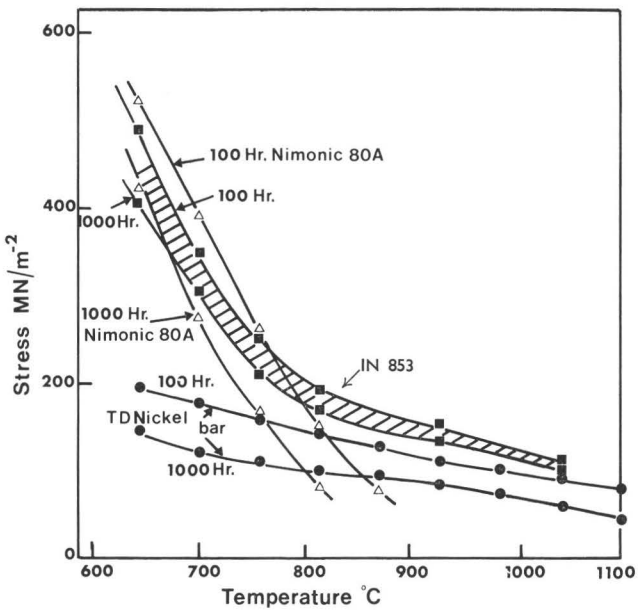

FIG. 6. — *100 hours and 1,000 hours rupture stress for dispersion strengthened superalloy compared with data for nimonic 80 A and TD nickel.*

directionally solidified alloys [25]. The need to improve strength at high temperature has also been partly fulfilled by processing developments which have taken two entirely different routes. As was pointed out earlier the strengthening phases in all superalloys dissolve at high temperatures leaving only solid solution strengthening, which is controlled by relatively heavy elements such as tungsten, molybdenum, tantalum, etc. What is needed is an inert dispersed phase which will be effective up to the alloy melting point. Prior to the introduction of powder metallurgy techniques this was not possible by conventional casting or forging routes and probably the best known material (and least used) utilising such an approach was thoria dispersed nickel (known as T. D. nickel), in which 2 % by volume of thoria was added by a rather complicated process. This alloy has excellent high temperature strength but is weak at low temperatures and also has little, if any, oxidation resistance. Precipitation hardening by $Ni_3(Al, Ti)$ cannot be carried out by this method so that the development of an agitation milling process (using powders) known colloquially as « mechanical alloying », which produces both inert dispersoids and precipitation hardening, represents a major advance for superalloys [9]. A commercially available alloy IN853 with the strength of Nimomic 80A below 815° C and that of TD nickel above 815° C is now made in a variety of forms and may well be the pre-cursor for a new family of superalloys.

The importance of this development is clearly shown in figure 6. Similar results have been obtained for cobalt-base alloys and if the promise of the latter group is fulfilled a significant step will have been made in the production of more economic grades of superalloy. A specific and most important feature of these alloys is the need for an elongated grain structure with a high aspect-ratio if good high temperature properties are to be obtained [26]. Recent evidence has underlined the high degree of process control which is required for the production of this microstructure. A high temperature heat-treatment is needed plus a critical amount of « stored energy » which is induced by the effect of the dispersoid particles on the thermomechanical treatment used to consolidate and shape the material. Since the milling process used to mix the metallic and non-metallic powders also « stores » energy in the powders, the subsequent heat-treatment requirements have to be clearly identified as a function of the milling time and the properties of the powder particles. A novel technique for producing this grain structure has been developed [27] using a solid state crystal growth process, known more colloquially as ZAP (zone aligned polycrystals). The non-recrystallised alloy is passed at a specific rate through a heated zone in which there is a steep temperature gradient. The alloy emerges from the temperature gradient with a strongly oriented recrystallised structure consisting of grains with aspect ratios of up to 15:1. In certain cases single crystals have been made. The stress-rupture properties at 1,100° C were doubled by this treatment. The use of powder metallurgy processes was initially introduced so as to overcome some of the segregation problems which are almost inevitable in large ingots of alloys which contain several elements. Each pre-alloyed powder particle is effectively a « micro-ingot » and hence upon consolidation by extrusion of forging a fully dense solid of uniform composition can be obtained. The design advantages of such powder processed alloys are significant: alloy melting temperature is increased; greatly improved hot workability; fine grain size which gives both strength and ductility at temperatures below about 900° C. Economic advantages which will undoubtedly arise from this approach include a better utilisation of material, since the use of a preform which has been compacted approximately to the forging shape will reduce forging costs, cut out expensive machining costs and conserve material. This is an important point since the material cost of a superalloy component is a very small fraction of the overall cost (an approximate figure for a 1 kg [illegible] blade costing £ 100 is £ 0.5 in material co[illegible]

The fine-grained state of powder alloys not only gives improved properties but it can also be made use of during processing. At temperatures of the order of half the alloy melting point, stable fine grained (less than 10 μm) alloy can be strained slowly at very low loads and superplastic flow is said to occur. A commercial process for making turbine discs out of a nickel-base alloy IN-100, which is unforgeable by conventional routes, has been developed with the curious name of « gatorising ».

The pre-alloyed powders, prepared either by atomisation or rotating electrode processes, are consolidated using hot isostatic pressure technique or hot extrusion. This results in a very fine grained, homogeneous, microstructure which, when strained at rates of 10^{-2} min^{-1} at temperatures in the range 900° C to 1000 °/, shows superplastic behaviour *i. e.* high elongations at low stresses. This can also be produced by compressive deformation in a forging process and by careful selection of the die material (molybdenum can be used) and design of the die shape, complex shapes can be made in single stage process. This is an interesting development, not only for its exploitation of unusual plastic properties but also because it illustrates the potential of powder routes for the direct production of shapes using alloys of closely controlled composition and conserving expensive material. The attraction of powder technology is further underlined by the possibility of designing new alloy compositions for powder processing routes and powder components. In this way specific properties such as corrosion-resistance, creep rupture strength, etc., can be obtained, even though they would be difficult, if not impossible, to produce in castings or by conventional forming processes. Dispersed non-metallic phases can be added without any danger of producing large deleterious inclusions and there is evidence that high volume fractions of such phases can be added in this way [29]. Large components have been made in large quantities using this technique and it will certainly figure in the future development of powder routes which will conserve materials and energy as well as giving improved properties.

2.3.3. **Processing for composites.** — The use of strong, stiff fibres to reinforce weak metallic or plastic solids is now well-known and composite materials are widely used in engineering design especially for resins containing glass fibres. High temperature materials which could utilise this principle would be of enormous benefit but attempts by conventional routes *e. g.* putting strong metallic fibres (W) into superalloy matrices, have not been marked with success, because of reaction between fibre and matrix. Ceramic fibres have also been used but although the high temperature strength properties are outstanding, the oxidation resistance of such metallic matrix-ceramic fibre composites is poor [30], mainly because of the high surface area of metallic phase which is exposed to the oxygen and nitrogen, which can either diffuse in via the ceramic phase of via the ceramic-metallic interface. The production of oxide phases at these interfaces disrupts the mechanical rigidity of the composite and they are thus only likely to be useful if they can be used in inert atmospheres or if they can be protected by reliable coatings.

A far more attractive method with the potential of commercial application utilises the fact that liquid

TABLE VI. — *Comparison of the metallurgical possibilities of melting/refining processes for high temperature alloys.*

	Primary Melting Processes					Secondary Remelting Processes			
	AM	AM+VR	AM+AOD	VIM	PAM	VAR	EFR	EBM	PAR
Alloy Flexibility	-	+	+	++	++	++	+	+	++
Alloying	++	++	++	++	++	-	-	-	-
Superheating	+	+	+	++	++	-	-	++	++
Refractory Interaction	-	-	-	-	(--)	++	++	++	++
Slag (Flux) Treatment	+	+	++	-	+	--	++	--	+
Composition Control	+	+	+	++	++	++	+	+	+
Removal of Gases	--	+	+	++	(+)	++	--	++	+
(Carbon) Deoxidation	-	++	+	++	(+)	+	-	++	(+)
Desulphurization	++	+	++	-	+	-	++	-	+
Decarburization	-	++	++	++	(+)	+	-	++	(+)
Volatilization (Impurities)	--	+	+	++	(-)	+	--	++	(+)
Microcleanliness	--	+	+	++	++	++	+	++	++
Solidification Control	--	--	--	--	--	+	+	++	++

Rating: + Good ++ Better - ( ) Probable effect

alloys undergoing a eutectic reaction can be solidified uni-directionally so that one phase can be caused to grow with a fibrous or lamellar morphology [31]. Because of the formation of fibres from the liquid state they are of low interfacial energy with respect to the matrix and hence are stable. An examination of the properties of the metallic elements shows that there are very few candidates for service at temperatures greater than 1,100° C and for this reason research is now being carried out not only on nickel-, iron- and cobalt-base matrices in *in situ* composites but also on intermetallic compounds which although brittle have much higher melting points [32]. As well as experimental investigations of potentially useful eutectic systems, there is now a considerable effort being made to calculate the range of existence of eutectic systems in multi-component alloy systems using a thermodynamic approach so that more rapid solutions may be found without unnecessary experimental work.

The mechanical properties of eutectic composites are controlled by the volume fraction of the reinforcing phase and the distance between the phases (in a manner analogous to that of the effect of grain size on yield strength as described by a Hall-Petch equation). The volume fraction is in turn controlled by the surface energy between the two solid phases and analysis [33] shows that a rod form occurs when the volume fraction is less than 32 % and a lamellar form at higher values. The fibres can withstand a higher elastic strain prior to fracture and are thus more efficient than lamellae. Against this however must be weighed the fact that fibres only form at low volume fractions and hence the overall composite strength will be lower than those measured in lamellae-reinforced composites. Stability considerations also tend to favour lamellae rather than fibres since they may withstand more severe thermal gradients and thermal cycling conditions.

Various methods have been employed to vary the

TABLE VII. — *Categories of* in situ *composites*
(*Lam* = Lamellar; *Fiber* = Fibre *and M* = Metallic component).

Ductile-Ductile

Alloy	Second phase			Melting Point, °C
	Composition	Form	v/o	
Ni-W	W	Fiber	6	1500
Ni,Co,Al-Cr,W	Cr,W	Lam		
Ni_3Al-Mo	Mo	Fiber	26	1306
Ni_3Al-Ni_7Zr_2	Ni_7Zr_2	Lam	42	1192

Ductile-Semiductile

γ-δ				
Ni-Ni_3Nb	Ni_3Nb,δ	Lam	26	1270
γ'-δ				
Ni_3Al-Ni_3Nb	Ni_3Nb,δ	Lam	44	1280
Hypoeutectic			32	1280
γ/γ' - δ				
Ni,Al-Ni_3Nb	Ni_3Nb,δ	Lam	~35	1272 to 1274
Ni,Cr,Al-Ni_3Nb	Ni_3Nb,δ	Lam	~33	1244 to 1257

Ductile-Brittle

Co-Co_3Nb	Co_3Nb	Lam	---	1270
Ni-Cr	Cr	Lam	23	1345
Ni-NiBe	NiBe	Lam	38 to 40	1157
Ni-Ni_3Ti	Ni_3Ti	Lam	29	~1300
M-MC				
Co-TaC	TaC	Fiber	16	1402
Ni-TaC	TaC	Fiber	~10	----
M-M_7C_3				
(Co,Cr)-$(Cr,Co)_7C_3$	$(Cr,Co)_7C_3$	Fiber	30	1300
(Ni,Cr)-Cr_7C_3	Cr_7C_3	Fiber	30	1305

TABLE VII *(continued)*.

Alloy	Second phase			Melting Point, °C
	Composition	Form	v/o	
Brittle-Ductile				
MO-M				
(ZrO_2,Y_2O_3)-W	W	Fiber	∿6 w/o	
(HfO_2,Y_2O_3)-W	W		∿12 w/o	
MgO-W	W			
Cr_2O_3-Re	Re			
-Mo	Mo		8.6	1760
-W	W			
Ni_3Ta-Ni_3Al	Ni_3Al	Fiber	35	∿1360
CoAl-Co	Co	Fiber	35	,1400
Brittle-Brittle				
Al_2O_3-ZrO_2		Lam		1870
Al_2O_3-(ZrO_2,Y_2O_3)		Fiber		1890
$Al_6Si_2O_{13}$-Al_2O_3				1840
NiO-CaO		Lam		1720
$MgAl_2O_4$-MgO_2	MgO	Fiber	>50 w/o	1995
ZrO_2-Y_2O_3	ZrO_2	Lam	6.38 w/o	
Fe,Cr-Fe,Cr,Nb	Fe,Cr,Nb	Fiber	22·1	1275±10

volume fraction of the phases [34] present in eutectics *e. g.* coupled growth of off-eutectic systems: monovariant eutectics: multi-variant and multi-component systems. In this way considerable compositional latitude is obtained and a satisfactory balance struck between properties such as high temperature strength and high temperature oxidation resistance, etc. Table VII [34] illustrates some of the compositions and categories (based on mechanical properties) of some *in situ* composites studied to data.

The equipment used to make these eutectics essentially requires a controlled solidification in a high temperature gradient (G) at a sufficiently high speed (R) for economic production routes, without losing plane-front solidification conditions and breakdown to a colony structure.

By utilising liquid metal cooling to improve the thermal gradient and hence increase the ratio of G/R faster production rates are possible than for simple radiation cooling in air.

In order that these materials should be cost effective it is important that the cycle time of a unit should be as short as possible but compatible with satisfactory structures being produced in a reproducible manner [35]. This means that high values of G will be required if the value of R is to be high *i. e.* fast processing rates. The gradient can be increased either by more efficient cooling *e. g.* liquid metal coolants or by increasing the liquid alloy temperatures. This latter possibility will create problems with the refractories and particularly with cores used to make hollow parts.

Two types of eutectic system with commercial potential have been developed in recent years: one based on the $Ni_3Al(\gamma')Ni_3Nb$ (δ) lamellar system in which the Ni_3Nb is the reinforcing phase [36]; the other using carbide fibres *e. g.* TaC in both cobalt-base and nickel-base alloys [37]. Their rupture properties are superior to dispersion-strengthened and precipitation hardened alloys as can be seen in figure 7.

As well as economic problems there are potentially more serious problems related to the thermal stability of eutectic systems with respect to thermal cycling and to temperature gradients, which may be set up in a cooled component [38]. Degradation of the structure and loss of properties can occur and there is a great deal of effort being injected into research programmes so that the response of *in situ* composites to these constraints can be assessed. It will also be essential for rigorous quality assurance procedures to be established, if reliance on these new composite materials is to be ensured for critical applications.

The oxidation behaviour of the composites developed to date have been dependent on the amount of chromium and aluminium in the alloy and the importance of an adequate level of protection at 1,000º C is shown in figure 8. It is almost certain however that some form of protective coating will be required for the first generation of *in situ* composites.

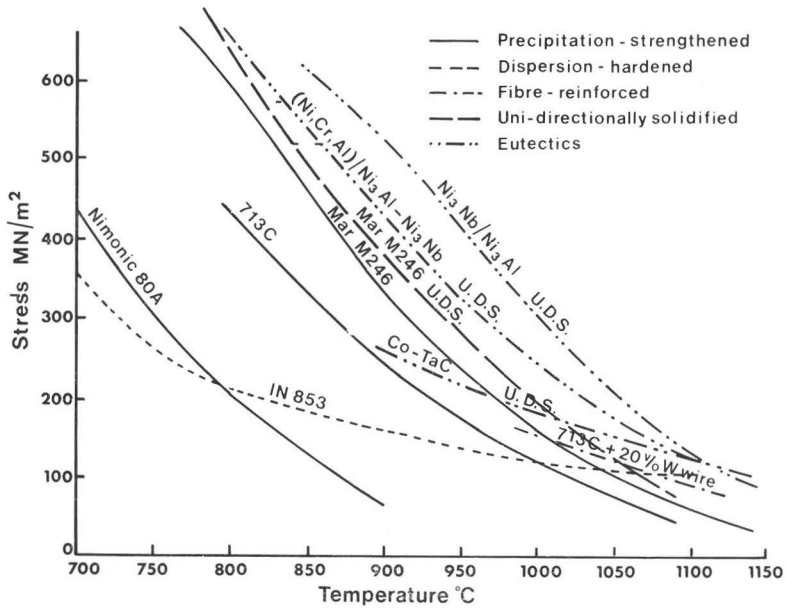

FIG. 7. — *100 hour rupture strengths of superalloys.*

At the time of writing trial quantities of nickel and cobalt-base alloys reinforced with carbides and intermetallic phases are being assessed and they may play a significant role in gas-turbine technology.

All of these process developments have taken place within the last twenty years and although they have occurred mainly in the field of aerospace technology, their impact outside this field may well be more extensive in the future. All of them cost money and the potential benefits, if such alloys are to be specified and hence prepared by these relatively novel processes, have to be assessed.

2.3.4. **Fabrication problems.** — Apart from these primary processing developments what else can the designer expect from these materials? More efficient utilisation of material is essential if greater economy is to be achieved and this involves processes which do not waste the alloys early in their forming. For this reason powder routes will certainly increase in importance as will the use of hot isostatic compaction to produce a shape as close as possible to the desired final form. An idea of the degree of utilisation of superalloy material during processing can be gauged from a figure published for aeroengines: out of 25,000 kg of starting material only 3,000 kg are found in the final product, taking into account the primary casting yield, forming and machining losses. The cost of machining is by far the most expensive item in the cost accounts for using superalloys. Machining is a difficult process since by definition superalloys are strong and tough and they can only be cut at speeds of about 5 % to 10 % of those used for common steels, and tool bit changes have to be frequently made [39]. As heat-treatment processes further improve strength levels, machinability deteriorates still further (machining in the un-heat-treated state is not possible because of the difficulty of maintaining dimensional tolerances) and with the trend to even higher performance levels this property will become an object of further attention from machine tool engineers. The most widely used processes depend on chip-making operations since they remove more metal at higher rates than un-conventional methods such as electrochemical machining. As can be seen from table V grinding is the fastest process and involves very high energy/unit volume of material removed (about thirty times more than for turning). Since the superalloys cannot be modified so as to render them more machineable (adding lead or a sulphide phase as is done for steels, is not practicable because of the high temperature service for which have been designed) two possibilities are available: develop new cutting tool materials or develop new processes, which will make the final object in a single operation. The cobalt-containing high speed steels have to be used for difficult machining operations *e.g.* broaching, drilling, as the superalloys are still hard when the conventional high

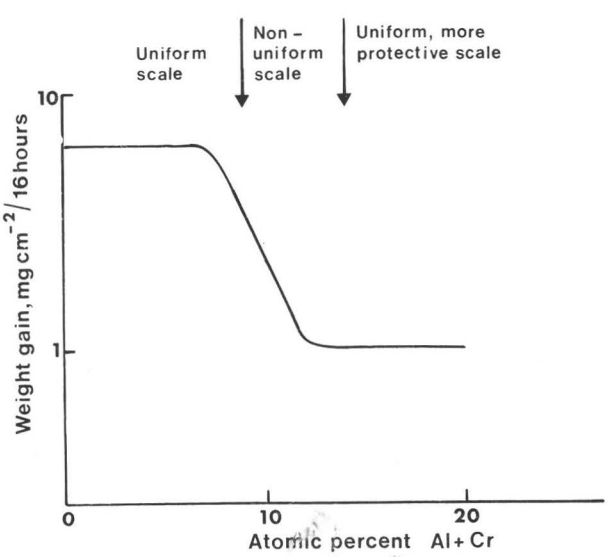

FIG. 8. — *Oxidation of composites at 1,000° C as function of chromium and aluminium content.*

speed steels start to soften *i. e.* about 600º C. The carbides are used for finishing operations such as face milling. Non-conventional processes have been developed for superalloy machining for several reasons: greater economy can be obtained; the workpiece does not degrade during machining (surface work hardening will occur with normal processes); unique shape requirements. The common feature of processes such as chemical machining, electropolishing, discharge machining, etc., is the fact that metal removed is independent of the mechanical properties of the superalloy. Developments at present being evaluated include the use of ultra fine-grained carbides in conventional compositions and newly designed compositions in which the cutting phase and matrix are selected and processed by powder routes. If inert oxides and nitrides with high hot hardness levels can be incorporated into a refractory metal binder then a revolutionary advance in cutting behaviour may well occur.

The drive to conserve energy, materials and hence reduce financial burdens will lead to more intensive effort in this area of final processing of a component.

The joining of superalloy components is not without problems, especially when the dispersion strengthened alloys are considered, since fusion techniques cannot be used as they destroy the alloy properties in the weld zone. Although welding has many drawbacks *e. g.* weld zone cracking; local mechanical property changes in the weld zone, in particular reduction in the ductility levels and fatigue limit; reduction in corrosion and oxidation resistance because of local compositional changes; it is still the most widely used fabrication technique for superalloys. Several processes are used including gas-tungten arc, resistance and electron beam and although they differ in detail their application always involves the minimisation of the heat input to the weld zone, so that cracking tendencies are reduced. The advantages of welding techniques are related to their low cost, low weight and retention of high strength in the weld zone and for these reasons welding will remain the most important joining method for superalloys, despite some of the drawbacks mentioned above.

3. REFRACTORY METALS

The superalloys have unique properties, which have, been vital to the development of high temperature processes. By controlling composition and developing fabrication routes, which make more economic use of the alloys, a wide range of applications have been.

The future will certainly see the further development of processes with as few steps as possible between raw material and final finished component, but the ultimate limit of superalloys is related to their melting point and to their ability to resist atmospheric attack above 1,200º C. Above this range two avenues can be explored: the use of refractory metals and the application of ceramic phases, and it is the former category which will be briefly analysed before considering some of the future developments which may occur in high temperature materials. Table VIII shows how the refractory alloys compare with superalloys, provided that their surfaces are protected from oxidative degradation. Their main advantages include much higher melting points, high moduli of elasticity and hence an ability to withstand much higher loads than superalloys.

TABLE VIII. — *U. T. S.* (MNm^{-2}) *at temperature.*

Alloy	1,100º C	1,320º C	1,540º C	1,760º C
Superalloys . . .	245/350	—	—	—
Niobium alloys . .	350	168	119	—
Molybdenum alloys.	630	385	252	182
Tantalum alloys. .	560	364	210	105
Tungsten alloys. .	700	420	280	210
Chromium alloys .	315	119	—	—

Unfortunately with the exception of chromium they have very high densities, which makes their use for rotating parts difficult to envisage particularly for tungsten and tantalum. In contrast to the superalloys the refractory metals have b. c. c. structures and hence have a ductile to brittle fracture transition at a specific temperature which is in excess of ambient. This presents an immediate problem to the engineer who has to design with a potentially brittle material even though they have adequate high temperature ductility values. Furthermore they tend to be embrittled by interstitial elements such as oxygen, carbon and nitrogen, which poses serious problems in obtaining high purity materials for commercially viable processing routes.

Chromium-base alloys are of potential interest since they have good oxidation resistance because of the formation of a protective Cr_2O_3 scale in a manner similar to that of the superalloys. They can be solid-solution strengthened with other refractory elements and further high temperature strength can be obtained by using dispersed phases such as carbides or nitrides. The most telling factor against chromium alloys is the effect of nitrogen on ductility. Amounts of nitrogen as low as 0.01 wt % can raise the temperature by several hundred degrees centigrade and despite several efforts to use rare earth elements to fix the nitrogen, it has not yet proved possible to protect chromium from embrittlement when exposed to air and thus give adequate design ductility. Unless a dramatic new development occurs it is rather unlikely that chromium alloys will be used in power generation units.

Molybdenum alloys were initially strengthened by dispersion of TiC and ZrC the alloys being known as TZM and TZC, but the realisation that HfC was more efficient and gave improved ductility values (10 % tensile elongation) in the swaged condition led to an increasing interest in Mo — Hf — C alloys. As with superalloys, significant improvements in high temperature strength have been obtained by using thermo-mechanical processing developments. By extruding the alloys at high temperatures (2,000º C) and then swaging at lower temperatures (1,400º C) an increase of 40 % can be obtained in the tensile strength (as measured at 1,350º C) to levels as high as 600 MNm^{-2}. In a similar manner, the tensile properties of tungsten can be impro-

ved although there are indications that minor compositional variations can lead to rapid coarsening of the HfC phase and loss of creep properties.

Despite these advances in strengthening (provided that oxidation is prevented) by processing developments, the poor low-temperature ductility of these alloys prevents them from being used on a wider scale. Purity levels have to be high *i. e.* low interstitial contents. Inert dispersoids are needed if a stable fine-grained microstructure is to be produced, and an expensive element, rhenium, has to be added if the so called « ductilising » effect is to be obtained.

A recent paper [40] has analysed the respective merits and demerits of the refractory metals and their alloys and it is suggested that there is still some realistic hope of improving their high-temperature strength and perhaps their ductility values. The most striking improvement is to be found in chromium alloys containing Ta, B and C which have strengths at 0.65 Tm (Tm = melting point) greater by a factor of 45 than that of high purity chromium. By optimising thermomechanical processing routes so that the strong dispersed phases are maintained in a fine and stable state, it has been suggested that further strength increases will become possible. This still leaves the thorny problem of ductility and it is evident that the effect of elements such as rhenium, iron, cobalt, etc., is worth exploring in greater depth particularly in terms of the possibility that the effect is related to the number of « *s* and *d* » electrons in the solute. All of this will come to nothing if the components are exposed to an oxidising environment, so applications will have to be limited to inert or reducing environments *e. g.* helium-cycle turbines or totally reliable coatings must be developed.

4. FUTURE TRENDS AND PROBLEMS

From a discussion of what has been achieved to the uncertain aspects of future trends presents certain difficulties, not the least of which is the reasonable likelihood that one will be proved wrong by future events. If the future is to be looked at in terms of both future demands and solutions to present problems then a sensible analysis can be presented.

Superalloys will most certainly be limited by their relatively low melting points, compared with the refractory alloys, to operational temperatures no greater than 1,200º C/1,250º C. They present problems of phase stability in isothermal and thermal-cycling conditions, which are likely to be all the more complex as long-term, maintenance-free, operation is required for high temperature components. This thus suggests that a useful line of research should investigate phase stability problems both in conventional alloys and in the newer directionally solidified eutectics and powder metallurgical products.

The problem of stability will involve diffusion information, phase analysis and the further development of phase computational techniques, *e. g.* (Phacomp) [41] based on the concept that bonding in electron compounds is promoted by electron vacancies in the 3d sub shell of transition metals. The technique has been used to predict the likelihood of certain embrittling phases being formed, based on an analysis of the composition of the matrix after major phases have been taken into account. The physical chemistry of multi-component, multi-phase alloys is not well understood and improvements in theory could well prove of great value. The interaction of fatigue and creep phenomena also requires further study and this should be carried out in conjunction with phase stability investigations so that the effect of microstructural changes on these failure mechanisms can be fully assessed. In addition to phase stability, the surface stability of materials must be studied in greater depth, for apart from some elementary guide lines, knowledge of the behaviour of complex, multi phase surface layers (formed either by oxidation or hot corrosion) is not very profound. In particular problems of oxide adhesion, hot-corrosion attack and the development of protective coatings with long lifetimes are worthy of attention. This applies with equal force both to superalloys and to refractory metals.

Processing developments have been at the centre of most of the recent technical improvements in power generation materials and it is in this area that further progress is likely to be made. By using both liquid phase processes and powder metallurgical routes it should be possible to design new alloys which have their compositions selected on the basis of a desired specific microstructure necessary for specific properties to be obtained.

The development of laser technology and its application to fabrication techniques *e. g.* cutting and welding and to surface alloying and heat-treatment will certainly be beneficial to high temperature materials. Their potential is significant and provided that multi-discipline programmes to develop systems can be successfully executed, applications will be found.

Similarly, processing developments can bring about the application of casting techniques to the refractory alloys which are fabricated at present by forging methods. The ductility problem of the refractory metals still requires an enduring solution which will allow their excellent high temperature strength to be usefully employed.

Protective coatings, if they can be replied upon, will also improve the chances for the practical exploitation of these alloys. These major problems represent a challenge to both the physical metallurgist and the engineer.

If this topic is reviewed at the 10th annual Petten Colloquium, then an assessment of the degree of success, which has been obtained, can be made. Or rather will we be assessing the advances made in producing ceramic engines as part of the next major advance in high temperature materials?

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Rev. int. Htes Temp. et Réfract., 1977, t. *14*, pp. 46-55

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CERAMICS FOR HIGH TEMPERATURE APPLICATIONS

By

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I. — *INTRODUCTION*

The kind of high temperature services requested from ceramic type materials, have traditionnally relied upon their chemical or chemo-mechanical properties. The most notable example is offered by the class of materials used as refractory linings in furnaces or installations where other materials are fabricated or shaped and treated. There is of course no *a priori* reason why other properties of some ceramic compounds should not be drawn from in high temperature environment. Such will be the case hopefully in the nuclear industry for example, but this type of ceramics and their corresponding problems will not be of concern in the present paper. Rather do we wish to focus our attention to a problem whose solution, which appears resonably likely although not certain yet, would be a significant technical achievement and have important economic consequences within ten to fifteen years from now. The question is: is it possible to design ceramic compositions and parts which can be used together with or in replacement for metals in high temperature applications where the property requirements are firstly mechanical and thermomechanical and secondly chemical, *i. e.* depending upon oxydation and hot corrosion resistance?

Much progress has been accomplished in recent years in the manufacture and property improvement of two groups of ceramic materials:

— *the glass-ceramics*, which result of the carefully controlled crystallization of pieces fabricated and shaped under conventional glass technology;

— the covalently bonded refractory compounds, most notably *silicon nitride and carbide*, which can be processed with a wide range of properties.

Both groups have been recognized to be potentially useful for mechanical service in the 1,000-1,600° C range and under oxydizing conditions, as would be the case in turbine engines of greatly improved efficiency with respect to the present day state of the art. The first group of materials, having compositions based on silica has temperature capabilities limited to about 1,200° C, with cordierite and spodumene type glass ceramics being probably the most promising, because of their low coefficient of thermal expansion and consequently their very good resistance to thermal shock. Although they should not be forgotten or neglected, it seems fair to say that the glass-ceramics which are under consideration for high temperature engineering applications, will benefit much from the experience gained on quite similar materials, used for more trivial applications, such as cooking ware and domestic utensils. These are beginning to be produced industrially in large quantities. Such is not the case of the highly performing silicon nitride and silicon carbide ceramics which still require considerable research and development efforts. The following discussion will therefore concentrate on these materials, after a few technico-economic arguments are recalled.

II. — THE CASE FOR A HIGH TEMPERATURE ENGINE

Earlier efforts to use ceramics in gas turbines and other high temperature mechanically loaded structures, some 15 to 20 years ago, failed primarily for two reasons:

— insufficient stress analysis procedures and techniques were available for calculating the magnitude and distribution of mechanical and thermal stresses that develop in complex geometries, hence no guidelines

could be given to the design engineers for extracting the best service of materials that were available then;

— fabrication methods and engineering properties of the materials themselves were not at a stage of development such that process engineers could produce sufficiently strong, corrosion-erosion resistant ceramics.

Both of these deficiencies have been, partially at least, overcome and the classical arguments which have usually been put forward in favour of the use of ceramics are still relevant today:

1. Reductions in engine weight and volume can be achieved, at constant power level, with respect to conventional internal combustion engines. Compared with an equivalent Diesel, the turbine weight and volume can be 40 to 60 % smaller.

2. Convenient and comfortable operation are to be expected for vehicles equipped with a turbine engine. No cooling circuit would be necessary, hence no precautions to be taken against frost. Heating can be made available to the passengers almost instantaneously. No gearbox would in principle be necessary. Practical operation however, will make one to be needed, but clutch can be omitted. Also, the absence of vibrations is a well known property of turbine engines because of the satisfactory mechanical equilibration of the overall structure. The average noise level can be kept some 4 to 5 decibels lower than what is commonly encountered in good Diesel engines, and noise fluctuations are small. The presence of a rotating heat exchanger, which is an economic necessity, also plays a favorable role in that respect.

3. Atmospheric pollution due to exhaust gases can be considerably reduced. No oil is consumed in the turbine; hence no smoke is produced. The combustion efficiency is high. There is a large air excess, virtually no carbon monoxide is sent to the atmosphere and of course no lead is added to the fuel. The oxides of nitrogen raise more problems since their concentration has a tendency to increase as the maximum cycle temperature is increased. It is generally agreed however, that appropriate modifications can be brought to the details of the combustion reaction which will satisfactorily solve this difficulty.

4. The chemical quality of fuel which would be needed for a turbine engine is also of importance since it bears an influence on the operating cost. Relatively low grade fuels, similar to those used in Diesel engines are acceptable. It is also a result of recent research studies that such impurities as Sulfur or Vanadium which have hot corrosion effects detrimental to the usual metallic alloys, would not be prohibited in engines made of silicon nitride and silicon carbide parts.

5. From raw materials cost and availability considerations, two decisive advantages are clearly apparent in favor of ceramics, over the currently used superalloys. First, silicon, carbon and nitrogen are abundant elements, quite evenly distributed on the earth. They are not strategic materials and no risk of supply shortening or cut off would be taken with silicon nitride or silicon carbide. The extraction of silicon and its metallurgy, and also the synthesis of the nitride and carbide in powder form, are well known industrial processes and no major difficulties would be expected at this stage, in the scaling up and quality control of powder production. It should also be noted that superalloys are much more expensive than silicon nitride or carbide. The cost ratio ranges from ten to about thirty, depending upon the kind of superalloy. The difference appears even greater when the latest high performance cobalt base materials are taken into account. Such an estimate is applicable to raw material costs only, since it is at the moment impossible to evaluate the incidence of ceramic shaping, sintering and finishing, because such questions are still a matter of research and development and also because the present day prices of commercial parts and components suffer from an overall insufficient production capacity to match the demand of all research and testing laboratories.

6. Finally and most importantly of course, the development of a higher temperature engine will bring both a higher efficiency and a lower specific fuel consumption as measured in liters/horse power per hour. This a well known direct consequence of Carnot's principle, and the increase of the turbine inlet temperature has been the major concern of designers and engineers in the field, for over thirty years. Enormous scientific, technical and economic efforts have been devoted to pursuing this goal. To day high turbine inlet temperatures can be reached, in part thanks to the development of very sophisticated air cooling techniques which of course draw from the compressor output. The corresponding reduction of the overall engine efficiency will consequently be the more severe, the more the temperature is raised for a given material. The ultimate limitation is close to being reached for nickel and cobalt base alloys. It follows that a completely new class of materials must be investigated, which must allow turbine temperatures to reach the 1,300-1,400° C range without blade cooling if the corresponding engine is to become competitive with the conventional Diesel.

III. — MATERIALS AND PROPERTIES

We shall not attempt to discuss or give a detailed account for the reasons which have led to the selection of silicon nitride and silicon carbide as the best candidates besides glass ceramics, for high temperature engineering applications of the type which we are considering here. The choice resulted from the consideration of a number of intrinsic material properties such as thermal expansion coefficient, refractoriness and thermochemical stability, and it has been generally accepted. this paragraph, which draws from a recently published Review paper (1), will briefly present the fabrication techniques and property evaluations of the materials, currently available from various commercial ceramic

(1) *Powder Metallurgy International*, 1975, [illegible] and 1975, 136.

producers. It is thus important to remember that whatever numerical figures are given, they have to be considered in relation to the present fabrication state of the art. Substantial progress is still possible, as we shall try to show below, which will undoubtedly be reflected upon the materials' characteristics. This is particularly true as concerns the engineering properties.

1. Materials fabrication and structure

Silicon nitride and silicon carbide ceramics can be fabricated in a variety of shapes and dimensions by means of either:

— high temperature vacuum hot-pressing,
— heterogeneous reaction-sintering,
— chemical vapor deposition.

The first method at the present time yields the more highly performing materials, especially at low and moderate temperatures. The second one it the most economically promising and versatile. The third one can in principle be adopted for making self sustaining objects: it would be very expensive and still necessitate important research and development efforts, although the resulting properties can be expected to be best possible. Chemical vapor deposition however, may successfully be used for upgrading reaction-sintered materials through the development of impervious, defect-free surface layers.

Vacuum hot-pressing. — Covalently bonded refractory compounds have tradionnally been considered impossible to densify by means of conventional pressureless sintering. It has been known for quite some time that Si_3N_4 [1] and SiC [2] respectively, can be hot-pressed under moderate loads, at high temperatures and with the aid of a small fraction of oxide additions. Typical microstructures are shown on figures 1 and 2. In both cases the nature and amount of the purposely added binder, as well as the residual impurities and the powder type (crystallographic modification) and size, play a dominant role on the evolution of microstructures and the final properties.

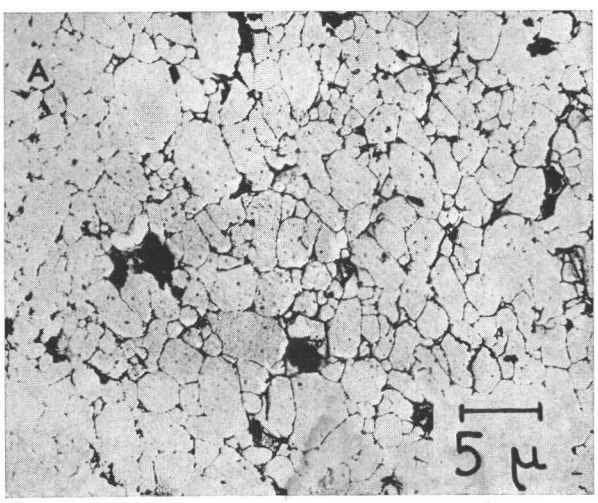

FIG. 1. — *Microstructure of hot-pressed and etched* Si_3N_4 [ref. 10].

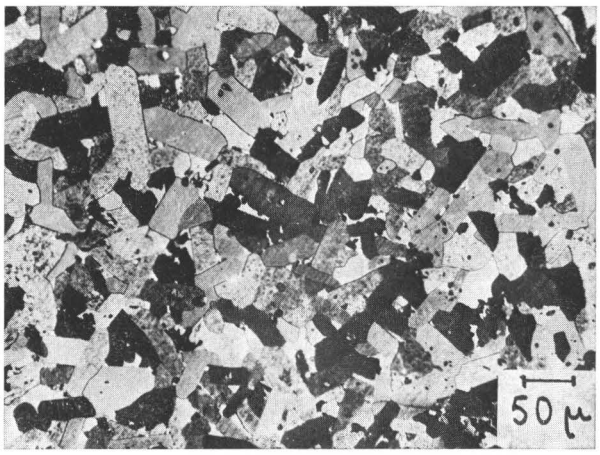

FIG. 2. — *Microstructure of hot-pressed and etched* SiC.

On the one hand, 3 % to 5 % MgO are added to $\alpha - Si_3N_4$, and the mixture is vacuum hot pressed at temperatures around 1,700-1,800º C. On the other hand, similar amounts of Al_2O_3 are added to hexagonal (alpha) silicon carbide and billets are pressed at or above 2,000º C. Microstructure evidence and high temperature mechanical behaviour of both ceramics, clearly show that liquid phases are present at the pressing temperatures, and cause densification by particle rearrangement and solution-reprecipitation mechanisms. These phases are glassy in nature and their viscosity gradually decreases as the temperature is raised. They consist primarily of the added oxide (MgO or Al_2O_3), the residual impurities (CaO, Fe_2O_3...) and some silica which is inevitably present, either in the starting powder or as an oxydation product, introduced during powder milling and handling. Obviously, the chemistry of the boundary phase will determine its viscosity and hence, play a dominant role on the high temperature mechanical properties.

It has also been found [3] and has remained insufficiently explained, that the high strength silicon nitride ceramics are only obtained when the starting powder predominantly consists of the α modification. The $\alpha \rightarrow \beta$ transformation occurs during hot-pressing. The material exhibits a bimodal grain size distribution (average grain diameter ~ 1 μ). About 80 % of the grains are equiaxed, the remaining 20 % being elongated in shape. The macroscopic properties of hot-pressed silicon nitride, also are anisotropic, *e. g.* strength is ~ 20 % smaller parallel to the pressing direction than normal to it. Commercial hot-pressed silicon carbide usually consists of various polytypes of α — SiC. It has an equiaxed grain structure with an average size of 0.5 to 2 μ or larger, depending upon the amount of binder added to the starting powder, and the pressing temperature.

Reaction-sintering. — Reaction-bonded silicon nitride and silicon carbide ceramics can be prepared according to the following reaction schemes:

$$\text{I} \begin{cases} 3\,Si(s) + 2\,N_2(g) \rightarrow Si_3N_4(s) \\ Si_3N_4(s) + 3\,Si(l) + 2\,N_2(g) \rightarrow Si_3N_4(s) \end{cases}$$

$$\text{II} \qquad SiC(s) + C(s) + Si(l) \rightarrow SiC(s)$$

In the former case [4], silicon powder compacts are nitrided in flowing N_2 or $N_2 + H_2$ mixtures. The operation usually is a two-stage heat treatment below and above the melting point of silicon. In the latter process [5], molten silicon is infiltrated into a compacted mixture of silicon carbide and carbon powders. It reacts *in situ* with the carbon particles to give « secondary » SiC which bonds together the « primary » SiC grains. The microstructures of reaction-sintered silicon nitride and carbide are shown on figures 3 to 5. In both cases, some unreacted silicon is present in the sample : ~ 5 % in Si_3N_4 and ~ 8 to 12 % in SiC. Residual porosity at the level of 15 to 20 % is inevitable in silicon nitride. It usually consists of two families of pores, the larger ones having diameters in the 10 to 100 μ range. It has been shown that the pore phase plays a major role on the strength levels which can be reached, both at low and high temperatures .It is thus important to exert a close control on its morphology. Similarly, a drastic drop is recorded in the strength of reaction-sintered silicon carbide, on melting of the unreacted silicon at 1,420° C.

In both materials, the minor phases are important for controlling the mechanical properties. Both materials also contain variable amounts of the α and β modifications, depending upon details of the fabrication which are not fully understood and whose influence on the properties has not been satisfactorily documented. Most of the Si_3N_4 grains are $\sim 1\ \mu$ in diameter but larger ones, up to $\sim 10\ \mu$ are occasionnally found. In silicon carbide, the primary α grains, typically 10 to 15 μ in size, are held together by an intimate mixture of Si and β — SiC, as shown on figure 5. The detailed chemistry of the reaction-sintering process is complex in both cases and still incompletely understood. Significant progress therefore can still be made on the fabrication and properties of such ceramics. This would be particularly interesting in view of the unique advantages of the reaction-bonding process: a large variety of shaping techniques prior to sintering can be used, enabling extremly complex shapes (*e. g.* combustion chambers) to be obtained, and machining and finishing costs to be minimized. Finally, considering the relatively low firing temperatures that are needed ($\leqslant$ 1,450° C for Si_3N_4; $\leqslant$ 1,600° C for SiC) it appears that the

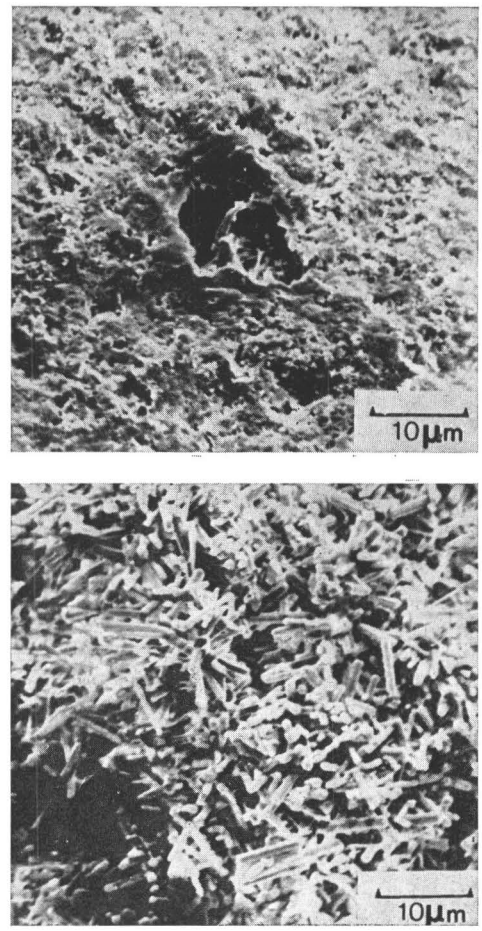

FIG. 4. — *Fracture surfaces of reaction-sintered* Si_3N_4 [ref. 11].

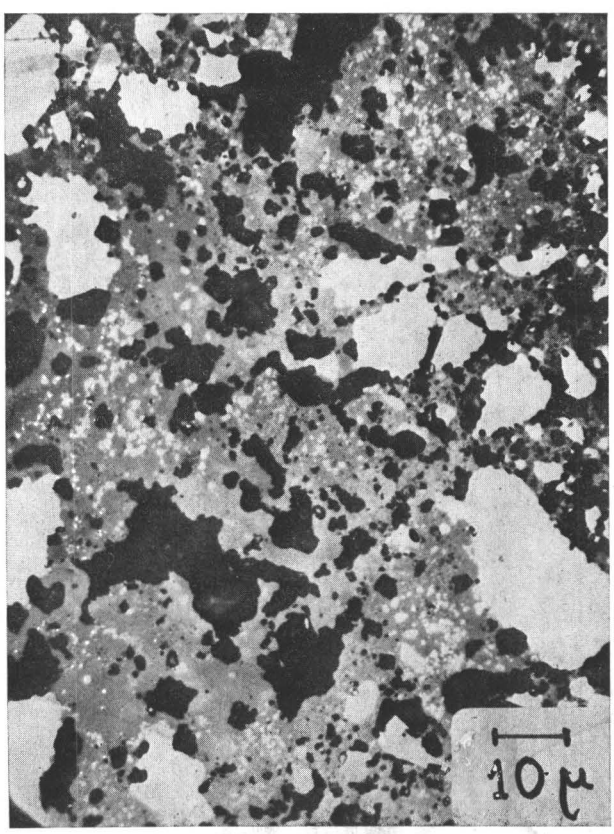

FIG. 3. — *Microstructure of unetched reaction-sintered* Si_3N_4.

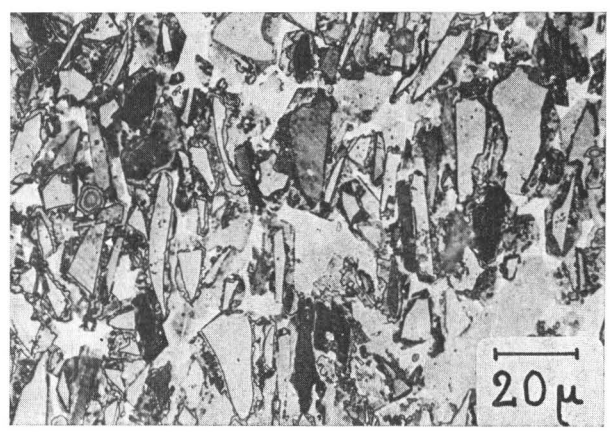

FIG. 5. — *Microstructure of etched reaction-sintered* SiC.

manufacturing cost of such materials can be brought and kept to reasonably small levels.

Chemical vapor deposition. — Silicon nitride or carbide layers having thicknesses in the 50 to 100 μ range can readily be produced on a great variety of substrates by pyrolysis of appropriate gaseous mixtures (usually $CH_3SiCl_3 + H_2$ for making SiC, and $SiCl_4 + NH_3$ or $SiH_4 + NH_3$ for Si_3N_4). The substrates are placed in a fluidized bed reactor or merely heated electrically. Submicron powders also can be prepared according to such reaction which then take place in a plasma flame fed with the gaseous reactants. The deposits and powders are either amorphous or microcrystalline. The grain size in the layers however, may be extensively varied by adjustment of the deposition conditions. Such a process is inherently expensive and raises technical difficulties, especially when wide or thick coatings are looked for. These however have quite beneficial effects on the substrate properties.

2. Mechanical and engineering properties

Most of the work that has been published up to now on mechanical and engineering properties of silicon nitride and silicon carbide ceramics, was devoted to:

— room and high temperature strength,
— creep resistance and slow crack growth,
— fracture mechanics and failure prediction,
— fatigue and wear resistance.

The oxidation and hot corrosion behavior also are of concern in high temperature engineering applications. It is generally felt in the present case however, that the intrinsic resistances of Si_3N_4 and SiC are quite satisfactory up to about 1,400° C at least. Microstructure and residual impurities (*e. g.* the intergranular glass phase in the hot-pressed materials) have been observed to dominate the oxidation behaviour of the ceramics. An improvement in oxidation and corrosion resistance is always noted as a side result of a modification in the fabrication procedure which brings about better mechanical properties. It then appears reasonable for the time being, to place a greater emphasis on the discussion of these properties and on their optimization.

Strength. — Strength is the most extensively investigated property. It depends on many factors including the testing method, strain rate, temperature, environment, impurities and microstructural features. The experimental measurements are usually carried under three point (sometimes four point) bending conditions. Only a few values are available on compressive or tensile strengths. The latter ones are usually smaller than those obtained in bending since a larger sample volume is subjected to the stress and the probability of a large defect to be present is increased. It has now become usual to try and establish relations between strength values measured under different conditions on a given material. The assumption was made that Weibull statistics adequately described the macroscopic behaviour of non ductile materials, and such relations were derived theoretically. Comparison with experiment showed quite good agreement for the various kinds of silicon nitride and silicon carbide ceramics in cases where environmental conditions and surface finish could be well controlled.

The machining of ceramics introduces surface flaws and defects and precautions must be taken in sample preparation before mechanical testing, especially in bending where the maximum of the stress is applied on the surface. It has been observed time and again that the apparent bend strength is substantially increased when the surface finish is improved and the sample edges are bevelled. It has also been observed that strengths of silicon carbide ceramics are much more sensitive to surface preparation than is the case with silicon nitride. This also shows what beneficial effects can and have been obtained from thin chemical vapor deposited coatings.

The temperature dependence of strength is shown on figure 6 for the currently available hot-pressed and reaction sintered materials. It is interesting to note that all exhibit roughly similar strength levels in the 1,200 to 1,400° C range, namely 30 to 50 hbars, whereas the hot-pressed ceramics are notably stronger at low and moderate temperatures. It may also be noted that silicon carbide appears to be stronger than silicon nitride at very high temperatures (~ 1,600° C) except for the reaction-sintered material which shows a drastic strength reduction at 1,420° C corresponding to the melting of the residual silicon. The gradual strength decrease of the hot-pressed samples has been related to the presence of a glassy intergranular phase containing most of the pressing additive (MgO or Al_2O_3) and the residual impurities of the starting powder. This phase is also responsible for the strain rate sensitivity which has been observed at temperatures above 1,200° C, where the strength is roughly proportional to the strain-rate, as a result of grain boundary sliding and sub-critical crack growth. Generally speaking then, the strength behaviour of the hot-pressed materials depends on grain-boundary chemistry (nature and amount of impurities as influencing the apparent viscosity of the intergranular regions) whereas microstructures (second phase inclusions, free silicon, size and distribution of pores) play the dominant role in both reaction-sintered Si_3N_4 and SiC.

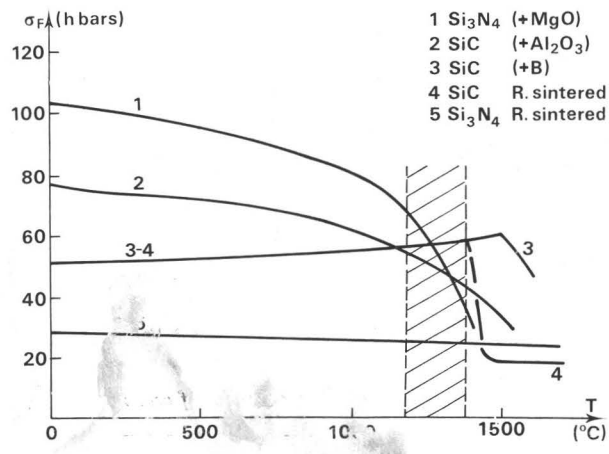

FIG. 6. — *Temperature dependence of bend strength.*

Creep and slow crack growth. — Comparatively fewer results are available on creep and slow crack growth than on strength especially for reaction-sintered SiC. The chemical and microstructural features which were found to bear an influence on strength, also affect the creep deformation and slow crack growth properties. In both hot-pressed and reaction-sintered materials, a grain boundary sliding mechanism seems to satisfactorily explain the observed behaviours, and extensive intergranular cavitation prior to sample failure. Recorded activation energies of 130-150 kcal/mole are also consistent with this interpretation since they closely correspond to those for viscous flow in most silicate glasses. The stress exponents usually fall between 1 and 2. The creep rates can be increased by two or three orders of magnitude if the concentrations of impurities such as calcium which lower the viscosity of the boundary glass phase are allowed to increase from the 100 to the 1,000 ppm range. These rates can be decreased conversely, if the sintering aid is adequately modified. As shown on figure 7, the steady state creep rates of commercial silicon carbide ceramics are smaller than those of their silicon nitride counterparts. It is also apparent that the reactiosintered materials compare favorably with the corresponding hot pressed ones. Reductions in the residual porosity of the former will bring higher creep resistance. Generally speaking, it appears reasonable to assume that the creep properties of silicon nitride and carbide ceramics have not been optimized yet.

Delayed fracture has also been investigated at high temperature and direct evidence for slow crack growth has been obtained, as previously mentioned. Crack velocities versus stress intensity factor have been determined experimentally for the hot pressed ceramics.

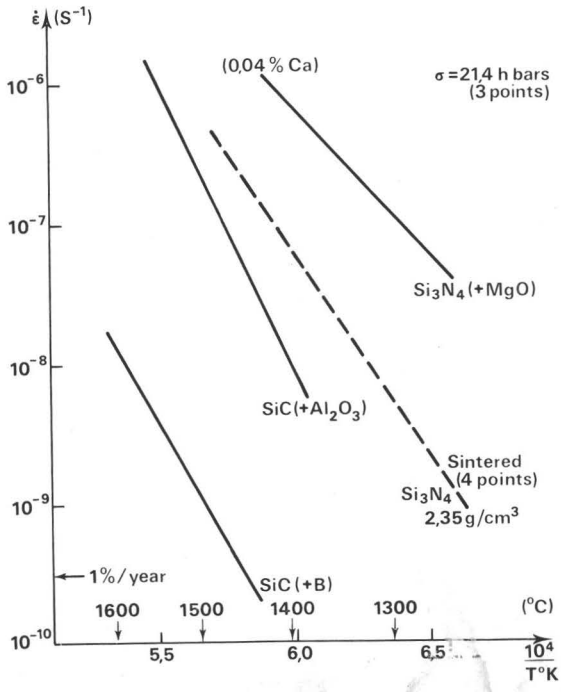

FIG. 7. — *Temperature dependence of creep rates.*

The empirical relation $v = AK_I^n$ was found to adequately represent the results at T $\geqslant$ 1,200° C, with A and n being constant for a given material and testing environment. The exponent n represents the susceptibility to subcritical crack growth. Typical values of about 10 ± 2 and 21 ± 3 where obtained for pure silicon nitride and silicon carbide respectively (1). The influence of testing environment on the high temperature mechanical behaviour has also begun to be investigated. Preliminary results suggest that for a given stress intensity, failure is somewhat more rapid in fuel combustion gases than in still air [6]. Impurities such as Na, Mg and V, if present in the fuel, do not markedly affect the corresponding failure time.

Fracture. — For all kinds of materials the critical stress intensity factor (K_{IC}) lies between 2 and 5 MN/m$^{3/2}$ at room temperature, which is comparable to values obtained on typical polycrystalline oxides, but about 20 times less than for conventional superalloys. So far, very little has been published on the temperature variation of K_{IC}. The only available information, on hot-pressed silicon nitride, shows a substantial rise at temperatures greater than about 1,000° C, up to a value of $\sim$ 12 MN/m$^{3/2}$ at 1,400° C Here again, the intergranular glass phase is thought to be responsible for this behaviour. As well as the stress intensity factor, the energy release rate of silicon nitride and carbide ceramics is small with respect to that for metals, and it is worth noting that the impact resistance of silicon carbide is substantially smaller than that of silicon nitride.

The development of statistical tools, essentially based on the Weibull distribution, and the knowledge of crack velocities in a given material, can give useful and realistic information about the life probability of a ceramic component under given service conditions. It has also become apparent that sensible structural design with ceramic materials will have to rely, at least partly, on proof testing procedures in the proper service environment, which can affect the high temperature properties. This last conditions results from the high reliability requirements which will be imposed in actual practice.

Fatigue and wear. — Very little is known to date on the mechanical fatigue resistance of silicon nitride and carbide ceramics. It appears from a study made on hot-pressed Si_3N_4 [7] tested in bending at 30 Hz, that the material life reaches 10^7 cycles for a 25 hbar stress at 1,250° C. The thermal fatigue however is somewhat better documented. The silicon carbide performances in that respect, are usually inferior to those of silicon nitrides processed similarly. Although a large variety of component shapes and testing conditions have been used, including simulations of gas turbines, the experimental observations are roughly consistent with existing theories for thermal shock and fatigue [8]. The large scatter which has sometimes been noted on the number of thermal cycles before failure in a given type of material seems to be attributable to scatter in

(1) Here again, minor amounts of selected impurities, *e. g.* Ca, can have significant effects on n.

the strength values, as resulting from microstructural or chemical heterogeneities.

Before closing this section, it appears worth pointing out that both SiC and Si_3N_4 are potentially useful materials for applications where optimized wear characteristics are required, such as in ball bearings. The good corrosion resistance and substantial high temperature strength are quite favorable properties in that respect. Very limited wear rates have been reported [9] at temperatures up to 600-650º C, for reaction sintered materials, slowly run against themselves or alloys such as Nimonic 90.

IV. — RECENT DEVELOPMENTS AND PROBLEMS

Although considerable progress has been achieved in a relatively short time on materials fabrication and processing, and on property evaluation and improvement, many problems remain to be solved before a reliable ceramic engine may be considered to be born. It is however important to keep in mind that most of the presently available information on engineering properties of silicon nitride and carbide ceramics, which we have just briefly reviewed, is by no means to be considered representative of the ultimate capabilities of those materials. In fact, it concerns what may be viewed as a « first generation » of the high temperature engineering ceramics, the fabrication and processing of which draws from at least a five to ten year old state of the art. Since then, research efforts have been continuing and increasing. It thus seems that a relistic appraisal of the situation in this field, must take into account, not only the known information about current commercial materials and problems, but also the recent research results. Some significant developments which occurred in the past two or three years will now be mentioned and a few important problems which remain unsolved will also be pointed out.

1. Some recent basic research

Several research programs have been undertaken, with the object of improving the high temperature strength and creep resistance through « minor » changes in the conventional fabrication processes. Some have already proved successful in the laboratory, others have even reached the developmental stage. In the hot-pressed ceramics, attention has been directed chiefly to the grainboundary glassy phase. Attempts to increase its refractoriness and/or viscosity include:

— reductions in the concentrations of harmful impurities such as calcium,

— post-fabrication treatments to promote crystallization of the glassy phase, together with composition adjustments in order to match the various thermal expansions in the resulting polyphase materials,

— modifications in the chemical nature and amounts of intentionally added sintering impurities. It has been possible for example to hot-press silicon nitride with Y_2O_3 additions instead of MgO. As a result, strength levels of at least 70 hbars are now attainable at temperatures up to 1,375º C.

In reaction-sintered materials, a better control of microstructure development during fabrication and of its reproducibility is the main objective. This is being pursued for example through:

— closer control of the shaping and reaction parameters, such as particle sizes and temperature profiles,

— systematic evaluation of impurity effects on the courses of reactions (kinetics, phase selection...) and on microstructures (porosity, pore size distributions...). This is particularly important in silicon nitride where minor amounts of oxygen in the nitriding gas are known to play a major role, incompletely explained yet, but which can be controlled by suitable impurities added to the starting silicon powder [17].

Two other recent research results can be considered of importance as they possibly open the way to what may be termed a « second generation of high temperature engineering ceramics »:

— The development of pressureless sintered SiC. — It has been a general belief that silicon carbide, and other covalently bonded solids could not be densified under conventional sintering conditions, contrary to most oxide materials. The physical reasons for this state of affairs remained unexplained until it was suggested [12] that this absence of densification is the result of too high a grain boundary to surface energy ratio in commonly used silicon carbide powders, which renders the process unfeasible thermodynamically, unless an external pressure is made available to add its effects to the surface energy and upset this unfavourable ratio. The upsetting of the surface energies ratio is also made possible by the combined action of small additions of carbon and boron to the original silicon carbide powder which presumably remove low surface energy silica layers and decrease the grain boundary energy as a result of preferential segregation.

All conventional ceramic-forming techniques, including die and isostatic pressing, slip casting, extrusion and injection molding can be used for preparing complex shapes, which is a decisive advantage over hot-pressing. The present practice necessitates a thermal treatment in the 1,900-2,000º C range to produce a ~ 95 % dense, fine grained body (fig. 8), and fairly stringent conditions are also imposed on the type and size of the starting powder, but not all of them may remain so. Preliminary results on the mechanical properties of sintered silicon carbide are quite promising since the high temperature behaviour of the materials is equivalent to that of the best hot-pressed ceramic. But most importantly it is now widely accepted that no fundamental reason *a priori* forbids the successful densification of other materials such as Si_3N_4, AlN, BN or diamond.

— The development of nitrogen ceramics. — Since Japanese and British workers made the surprising discovery that substantial amounts of aluminium and

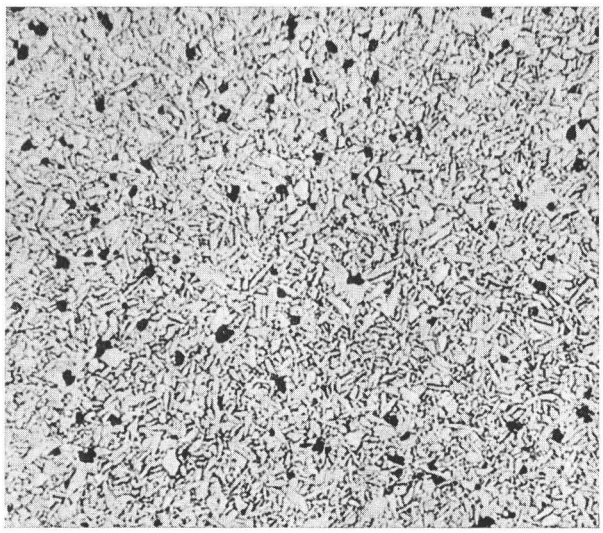

FIG. 8. — *Microstructure of pressureless sintered* SiC [ref. 13].

oxygen could substitionally dissolve in the $\beta - Si_3N_4$ lattice, the existence of quite a broad class of new nitride and oxynitride phases has been either postulated from crystal chemistry considerations or experimentally prepared [14] as is examplified on the diagram of figure 9 for the Si — Al — O — N quaternary system. These « sialon » materials, especially those having the $\beta - Si_3N_4$ crystal structure, are currently the object of substantial research efforts. They offer the advantage over « pure » silicon nitride, that single phase materials are in principle easier to prepare since impurities such as SiO_2 may be accomodated in the solid solution in combination with AlN which is purposely added (fig. 9). It has also been reported that these oxynitride solutions can be densified using conventional shaping and firing techniques, as well as hot-pressing. Their chemical inertness towards many molten metals including iron and aluminium alloys incidentally, may open up new possibilities in the process metallurgy of these metals, which would mean somewhat different applications than high temperature engines. As for their mechanical properties, only very limited information is available, suggesting that a whole spectrum of behaviours may be obtained depending upon average composition and processing details. It has been claimed [15] that some sialon materials have as good creep resistance, high temperature strength and oxidation behaviour as those of the best hot-pressed silicon carbides. These ceramic alloys are still in infancy, their potentialities are far from having been clearly evaluated and for the time being, there is no reason to believe that they should not acquire as much importance as the nickel alloys did and still do enjoy.

2. Pending practical problems

Before closing, it may be useful to come back to our initial problem, and make a few practical comments about some important questions, besides material fabrication processes, which still need significant research and development work of an applied type, before ceramic engines can be made to work economically. It is not our purpose here to give a critical assessment of the present status and prospects for any particular project. Such information may be found elsewhere (see for example ref. [16]). It is therefore well-realized that some of these comments at least, may already be or are likely to become obsolete in the future as a result of continuing research progress in the field, not all of which is readily or rapidly published. It is hoped however that they may also be useful as a frame for the follow-up of new developments.

It is generally agreed that the successful demonstration of an efficient high temperature gas turbine depends first upon the successful operation of its essential parts. These can be listed as follows in order of increasing difficulty with respect to material requirements and reliability: regenerating heat exchanger, combustion

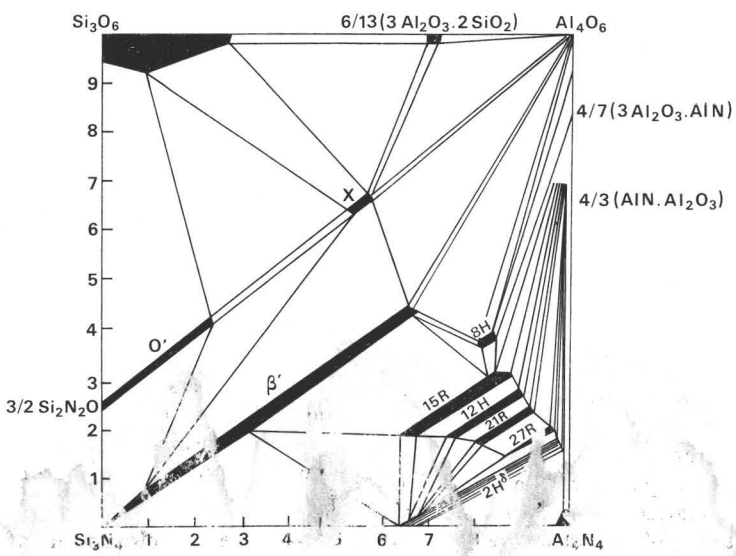

FIG. 9. — *Oxynitride phases in the* Si — Al — O — N *system* [ref.

chamber, static turbine vanes and rotating turbine blades. A number of progress reports have been issued so far, claiming encouraging or satisfactory operation under simulated or real service conditions of one or several of these separated engine subsystems. But to the author's knowledge the present day materials still have insufficient properties with regard to the rotating blade requirements, and no ceramic rotor seems to have sustained a real hot spinning test as yet. Better and cheaper fabrication processes and/or more highly performing compositions are needed.

Finally, it is important to keep in mind that major difficulties are and will be felt when engine parts are all separately considered to perform satisfactorily. It will then be necessary to join and assemble into a working unit, components fulfilling various duties, being of different chemical natures (ceramics, metals) or having varied properties and structures (hot-pressed versus reaction-sintered ceramics). « Simple » questions such as the attachment of ceramic rotors to metal discs for example, although very applied, still require a good deal of research on materials, on metal-ceramic joints and on ceramic-ceramic joints. Some of these questions may be solved in an acceptable way by the design of mechanical seals of optimized geometry. It is realized however that the development of a body of knowledge about chemical joining, either in metal-ceramic systems: SiC and Si_3N_4 on cast-iron and nickel alloys, or in ceramic-ceramic systems: SiC on Si_3N_4 and hot-pressed on reaction-sintered materials, would be highly desirable. In view of the peculiarities of the materials involved, it still does not appear clearly what part of the previous experience on ceramic to metal sealing will be applicable and useful in the present case.

CONCLUSION

The main purpose of this paper was to draw attention towards problems related to Materials, their fabrication, properties, handling, and some of the ways in which these can be improved. As a consequence, very little has been said about structural design with brittle materials, that is materials which exhibit almost complete absence of ductility and very small fracture toughness under tensile conditions (low K_{IC} values compared with metals of equivalent strengths). It is the author's opinion here that a lot, but not everything, may be requested from the materials engineer and the ceramist. More specifically, it is for the materials development specialist to produce in as economic a way as possible, components having satisfactory strength, creep resistance and so on, and for which property degradations due to differential thermal expansions, phase changes and the resulting thermal stresses, have been brought to a minimum. But it is not realistic to request that he eliminates the unpleasant consequences of the absence of ductility in ceramics. Although some actions may be taken, such as the incorporation of suitable fibers or other energy absorbing phases, it is inevitable that design engineers learn how to successfully cope with brittle materials. This necessitates :

— highly refined stress analysis methods, essentially base on finite-element calculations,

— the generalized use of component proof testing to truncate property dispersion curves,

— the systematic use of statistical methods to correlate the failure probability of components submitted to complex loading conditions, with the results of more straight forward proof tests,

— the verification of the design method, through a limited number of real tests carried up to failure.

It is fair to say that such a change of philosophy towards an increased sophistication has already been undertaken by design engineers of mechanically loaded structures in their search for higher efficiencies, as a result of the introduction of higher strength metals, usually having lower ductilities. Such a change still needs to be pushed forward and amplified in order that short cuts be avoided in structural design with ceramics. If due attention is not paid to this fundamental aspect of the problem, then it is virtually certain that, no matter how good the materials appear to be, failure will occur. Such a failure would inevitably introduce another ten or twenty year delay in the development of brittle material technology.

* * *

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ACKNOWLEDGMENTS. — Thanks are due to the *Direction des Recherches et Moyens d'Essais (D. R. M. E.)* for financial support.

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DISCUSSION

SECTION 4

C. D. Desforges. — I would like to comment on Dr. Whittle's observations dealing with beneficial effects of the rare earth elements which, in my view, is very important. One of the things we are concerned with in high-temperature technology is phase stability, whether this phase be within the matrix producing strength or a phase at the surface which has to be stable to give protection. I share Dr. Whittle's views that the effect is not only important but is also general. I have been concerned now for approximately the last nine years with my research group looking at some of the problems associated with rare earth elements. We have shown quite clearly that the effect can also be obtained by depositing the rare earth element at the surface by vaporization or from salts in solution. As Mr. Ubank explained, we can add the rare earth element to the melt and obtain the same effect, and we can also now incorporate it as an oxide thanks to processes such as mechanical alloying. We can incorporate the oxides so that one gets not only a strengthening effect but also this « adhesive effect » of the oxide scale. But we have also noticed that after very long term exposure some of the oxides are obviously not as stable with respect to the matrix as others, and the effect can deteriorate with time. I think this is very important, because one is going to be concerned with stability problems over very long periods.

Turning now from oxidation to hot corrosion —in some very recent work we have shown in fact that the rare earth dispersoids, in oxide form, work very efficiently indeed to improve the hot corrosion resistance of nickel base alloys. I think this is very important, because a possibly unjustified criticism that is often levelled at nickel based materials is that their hot corrosion properties are not as good as cobalt, and this seems to me to be a very good way of improving them.

Finally, we have also demonstrated that it is also applicable to iron based systems. There is quite a potential for iron based super-alloys on a cost basis, and thanks to powder metallurgical processing there is some reasonable hope that by adding the rare earth oxides one can obtain strengthening improvements and surface stability to hot corrosion and oxidation.

W. Betteridge. — Can I just add to what Dr. Desforges said that the rare earth elements can be incorporated to have a favourable effect merely by surface coating. We had a very marked effect of cerium added by dipping electrically heated wires into a simple cerium nitrate solution. We get a very thin film of oxide, and it makes an amazing difference to the coherence and adherence of the surface scale formed in air. That is a very easy technique for looking at the effects of different oxides.

D. P. Whittle. — Dr. Betteridge, is there not a difference between an oxide dispersion and a rare earth element dispersion in that you do not get all the benefits of the rare earth addition when you add it as a metallic element as opposed to adding it as an oxide dispersion ? One of the benefits that you get with an oxide dispersion is that you can form the protective oxide at substantially lower chromium contents than you need in the absence of the dispersoid, whereas this is not true, if you add it as a reactive element.

W. Betteridge. — I agree with what Dr. Whittle says, and if you incorporate the oxide as a dispersion in the alloy you have a continual feed into the scale as it is formed, whereas if you put a surface coating on, although you can replace it from time to time, you cannot do so continuously.

L. W. Graham. — I would like to return again to the question of cost effectiveness in order to make some decisions about what kind of work should be pursued. We heard the suggestion yesterday from Dr. Edeleanu that one should turn more to a gas turbine kind of application in the power generation industry. I would like to ask therefore two questions. What is the life time of a combustion turbine, and what is the incentive to improve that lifetime? How much money do people here believe it is worth spending on that and over what period of time?

R. Ubank. — As far as cost effectiveness and lifetime are concerned, we are still in the stages of evaluating these new coatings (the overlay coatings), we hope for advantages of at least two times from the vacuum vaporated route. At the moment we are getting something like 3,000 to 4,000 hours from a standard pack of laminated coating.

L. W. Graham. — You are talking about an aircraft engine. But if we are talking about large scale energy

production, I am really raising the question how long can one envisage operating say a combustion fired power generation system today with the impurities from coal or oil combustion gases to drive the turbines.

R. UBANK. — For very long lifetimes and big engines (rather than aero engines with light structure), I think we tend to go to the new superalloys. The higher chromium superalloys will be used for the big blade construction rather than coatings.

I. KIRMAN. — Dr. Graham mentioned costs and, as always, there is no simple answer. But I think there is a point that is worth making in this context. My own laboratory is in the process of attempting to commercialize an alloy which offers considerably increased chromium content to those of the alloys that Dr. Ubank mentioned. The development costs of these alloys to us (and it is not a major step forward, it is using essentially existing technology in a novel way) has been 1/2 million pounds to date. That is the cost of developing in an industrial laboratory an alloy for this kind of application. The high cost occurs because as soon as you start increasing the life of the material, you have to increase the life of the testing procedures which you undertake to develop the material, and the cost of long life creep tests and associated tests is getting disproportionate to the benefit to the industrial laboratory of developing those materials.

W. WATT. — Dr. Whittle, I believe, mentioned pyroceramics as a possibility for high-temperature materials. I do not think this is possible. Pyroceramics are recrystallized glasses, and as you heat them, the cristals dissolve. You might think that you could make strong fibers out of pyroceramics, but again this is not possible, for if you make fibers out of the pyroceramics and cristallize them, the size of the crystallites is about the same order as the diameter of the fiber, in fact it is very weak.

Referring now to ceramics in general, I have three points to make and perhaps Mrs Anthony might be interested to comment. First of all, all materials made by man have got flaws in them, and ceramics I think have got more than most. I think there should be some mention of the strength of the volume under tears. This is a bit of data which seems to be missing especially for the high-temperature materials that Dr. Whittle was talking about, silicon nitride and silicon carbide. I think we should see the effect of volume size on strength. Thermal shock is always a problem with ceramics, and it can occur by a very quick heating which may not enter into many of the long term applications we have heard about during this conference, but nevertheless you can get a thermal shock were you have got a ceramic within a steady state with a temperature gradient through it such as an insulating liner in a duct. I feel that the effect of temperature gradient at steady state should be investigated for ceramics and also what are the initiating points of the cracks that could very well be the flaws.

The last point I would like to make, is the question of impact. People think that you might be able to reinforce ceramics with fibers and get something useful. Well, this is not so obvious as it looks. First of all, you must get good bonding from the ceramic matrix to the fiber, if you are going to transfer load into the fiber. And if you want to get increased strenght, this means you have got to have a modulus difference. To get good impact resistance, you have got to have a mechanism for absorbing energy, and the only possible mechanism absorbing energy in a fiber reinforced ceramic seems to be a debonding mechanism. So I would not hold out too large hopes for ceramic fiber reinforcing the ceramic.

C. EDELEANU. — I tend to disagree with you, Dr. WATT. The metallurgist introduced two gifts to the engineer. One is ductility, the second is impact strenght. Before the metallurgist came along, the Egyptians and the Greeks knew how to build things. If we are going to use ceramics, we have to reconsider basic engineering technology and design in terms of compression like the Egyptians and Greeks did. Now do not consider this is entirely impossible. The progress we made for instance in using ceramics for insulation has taken this sort of step in considering how one can design engineering components basicly in compression. I suspect that Petten could, before it goes too much down the line of the traditional metallurgist, think afresh in engineering terms and start thinking how new methods of design can be introduced to use ceramic materials to best advantage.

S. F. PUGH. — Now that is a good point. In fact, the concrete pressure vessel is one example in which the concrete is entirely in compression. Presumably if we had gas turbines with the blades joined to the outer ring, then at least they would not have a high tensile stress in the fibers. But nevertheless, there has been a certain amount of work done on fibers in ceramics. Rather than trying to get more strength, one is trying to get better fracture toughness by putting in crack stopping features.

C. EDELEANU. — To this I agree, but I am trying to draw the attention to the fact that this is trying to mimic one of the properties which basicly does not exist in these materials. I do not say stop this work, but the real advantage would be not to demand this property from ceramic materials.

A.-M. ANTHONY. — I agree with you, and I think the problem of ceramics is that it is a very old science since the beginning of the ages, and it is difficult to become modern. I want to generate some appetite for research on ceramics. I know of a motor, made in all alumina for an experimental car; this is a spectacular result. Another spectacular result is known from a medical application. Artificial bones have been made from stainless steel. Now we make it from alumina, because alumina is so porous that the bone grows again inside the pores. I think it is a spectacular improvement. So I feel in the future we need some metallurgists looking with a new eye at materials like ceramics.

I. KIRMAN. — Two comments I feel I ought to make following Dr. Desforges' paper. I think a note of caution

ought to be sounded that most of his examples are from the glamour end of the industry and should not be considered as being the run of the mill of high-temperature materials. I illustrate that note of caution by referring to the mechanical alloying development that has been going on for some years in International Nickel. It will be a long time before International Nickel will recover the R and D investment required to develop this process. The other point I want to make refers to Dr. Desforges' mentioning that the hot corrosion behaviour of cobalt is somehow superior to that of nickel. Good hot corrosion behaviour of both sorts of alloys is principally due to the beneficial effect of chromium. All the information that we have to hand shows that at equivalent chromium content the hot corrosion resistance of nickel based alloys is at least as good as that of cobalt based alloys.

C. D. DESFORGES. — I fully accept Dr. Kirmans' point on my deliberate selection of the « glamour » developments, which of course was not made for a glamourous presentation ! I fully appreciate that there will be both tremendous costs and a lapse of time perhaps up to 10 years before some of the laboratory developments I described become practical realities. I was trying to select developments, which I thought were significant, to demonstrate that process development is one very clear way forward in improving the performance of high temperature materials.

Turning to hot corrosion resistance: results indicate two specific features. The first one is that a great deal of the data on hot corrosion and oxidation resistance of components as opposed to samples, are obtained in rigs which vary from site to site. The specific thermodynamic potential and the kinetics of the processes are varying from rig to rig. Our experience suggests that an essential step to the solution of this problem is to have correct comparative test data.

The second: I think Dr. Whittle made the point that a lot of the testing is being carried out at too high temperatures; with reports frequently saying that « nothing is happening at 900° C ». When one drops to temperatures as low as 750° C, there are very serious corrosion problems as there are a few alloys that do not corrode and many that corrode drastically. It is clear that a rigorous examination of this serious problem is required.

M. VAN DE VOORDE. — During these two days a lot has been mentioned on the austenitic steels, on the nickel base alloys, the cobalt base alloys, etc. Not so much attention has been given to the refractory metals and alloys. Is there no real interest compared to the others, and which are the critical problems? I think that perhaps Prof. Kofstad could give us some information on this question.

P. KOFSTAD. — I am not sure I can give a complete answer, but I guess they are just too prone to oxidation and corrosion to be of much value today. I do know that a number of coatings, particularly silicide coatings (I think Dr. Whittle mentioned them) have been developed and are now in use and all very effective, but I guess one always lives with the danger that one may have cracking of these and that this may result in a catastrophic failure. So unless we can develop a reliable coating system with self repair capabilities, I would not place my bets on the refractory metals right now.

S. F. PUGH. — When talking of high-temperature materials and crack growth under creep conditions, obviously the particular mathematical trick of linear elastic fracture mechanics is not relevant at all. Nevertheless the treatment of crack growth under creep conditions is important, including analysis of the stress field around the crack, particularly towards the crack tip, the tensile stress field, the shear stress field, the relation to the creep properties of the material and the extent to which the rates of growth of flaws in a material at a high temperature can be rationalized. It is now becoming quite common practice in the case of plant operating at low temperatures to assess the effect of the presence of flaws on catastrophic failure, and on crack development under fatigue conditions. At high temperatures this is a newly developing area of science. I think it is right to record that this is an important and new area of study in materials operating at high temperatures. Of course we have also to take into account the important effects of the environment.

G. IMARISIO. — In this respect I would like to call to your mind the new techniques of failure analysis and failure prevention. In one of the first papers presented at this meeting failure prevention was one of the important aspects in combination with nondestructive detection of failures. This is a point where the nuclear and the non-nuclear industries join quite easily because the needs are the same. Unfortunately the background, the techniques of analysis, are only now under development, and it is quite difficult to have at hand practical data of reliability which can be used in analysis and prevention of failures. Colleagues are working at Ispra in a small part of this broad field of failure prevention and analysis. I suggest that this subject should be included in future research and development because this can help to join the interest of industry and research. In fact actually the design engineer is obliged to use uncertainty factors which can better be defined as ignorance factors (ignorance *e. g.* of the phenomena involved in rupture) and this obliges him to use more weight, more thickness, over-dimensions. If therefore the common view of defining failures as probabilities can become practice, then perhaps a common ground could be reached which could be useful for both engineer and research.

R. A. U. HUDDLE. — An important point to discuss at the end of this colloquium is how do we get new materials into industrial service, not only from the legal point of view, but also because you have to get them before safety committees. You may be interested to know that the chemical industry in a certain country is going to be saddled with the same sort of regulations that the nuclear industry has.

C. EDELEANU. — Certainly no material can be used by the engineer in a routine fashion until it has been

codified. It is physically impossible, it is not a matter of legislation, it is a matter of communication between your supplier, your designer, your inspector, your seller, your buyer, etc. So every material which has not been codified and any design which is not according to a code is a major problem. You have to use the short hand language of engineering and that is codes. On safety there is no basic difference. No industry is allowed to kill people or inconvenience people and no industry is above the law.

W. BETTERIDGE. — There are many applications which require no coding at all. I can well imagine that a new electrical resistor element could readily be put into industrial furnaces, if the manufacturer and the customer were each satisfied that it was going to meet their requirements. There is no insurance or design code in such applications that has to be met, and certainly many materials in these sort of fields are commercially very important.

C. EDELEANU. — Do you remember ever to have been able to sell a product to us without a specification, it might not be a national code but that shorthand language or specification which I include in the word « code »?

R. A. U. HUDDLE. — I am so glad this question was answered in this way. When one is dealing with a new product, it is a matter purely between the designer, the operator and the appropriate licensing authorities. If it has not got an ASME code, it does not mean you cannot use it, and I think this is going to be very important if for example we want to apply modifications.

M. VAN DE VOORDE. — I would like to compare papers, given at this colloquium, concerning the chemical and nuclear industries. In the nuclear industry codes are very severe but, by comparison, the chemical industry's codes are not so demanding and this, I feel, is reflected in the respective materials research programmes.

S. F. PUGH. — If I could make two comments about codes.

I think most people on the design side realize that in the United States severe difficulties have arisen over the problem of designing in the creep range for metal structures. In fact the Clinch River fast reactor project has been brought to a complete halt because of the needs for doing 3-dimensional time dependent finite element stress analysis on plant which is in the creep range. Therefore some people are even saying that fast reactors must now operate at temperatures below what ASME code regards as the creep range for austenitic and ferritic steels.

The second point about codes is that you can of course always build a plant on special argument. Even in the United States this is possible, it is tedious but it can be done. The codes are drawn up with much compromise and vagueness in the difficult areas.

The chemical specifications of alloys are vague in the extreme to such an extent that *e. g.* typical ferritic steel can be supplied according to ASME code and contain no iron whatsoever, it can be 90 % chromium and still conform to the code. You can have 1/2 % copper completely free of charge in your steel and very often you get 0.6 % nickel and you do not have to pay for it; they are not in the specification, but the specification does not say they must not be there. If you are interested in embrittlement, this could be very important. If you are interested in aging in service, the 1/2 % copper that you get free of charge can be extremely important.

H. SCHUSTER. — I would like to touch another aspect regarding the influence of code development on our work. Whenever a code is formulated, the material properties with their relevant ranges for the application of the code have to be defined. This is very important for the materials people: They have to know which parameters are most relevant in order to get a material finally approved and which amount of data must be supplied. It would be a great help for our work, if we had some idea which type of code we may expect for new regions of temperature, stress or corrosion. I would strongly recommend to establish an international center which develops guidelines for these codes in mutual and well organized communication with research and design. The work should help to define the national (or European) codes and guide the evaluation of material properties relevant for design. Maybe Petten can help here.

R. A. U. HUDDLE. — My experience of coding (particularly thinking of Windscale, Calderhall and that lot) is that it is the design team that has to decide what are the failure mechanisms. It is the people leading the project that have got to sort out the failure mechanism and specify really the materials.

S. F. PUGH. — Dr. Schuster mentioned that the code should give you some idea about what you need to know about the material before you can use it with any degree of confidence. But of course the ASME codes give you no guarantee about performance in service. They only guarantee that the plant as delivered: There is no mention of aging or any other form of deterioriation in service.

In fact Dr. Grosser's list gives you a whole list of things you need to know about a material before you can predict successful use in service.

The alternative is to try the material in an actual prototype plant. This is usually much quicker and is the way most engineering progress is made.

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FIRST PETTEN COLLOQUIUM ON ADVANCED HIGH TEMPERATURE MATERIALS: TECHNOLOGICAL AND INDUSTRIAL ASPECTS

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Le Directeur de la Publication : J. TALAMON

Masson, éditeur. Paris. — Dépôt légal : 1977. — N° d'ordre : 5051. — 1er trimestre 1977
Imprimé par Imprimerie Barnéoud S. A., à Laval. — 7302. *Commission paritaire :* n° 41753
Printed in France. OJD Diffusion 1974 (3/7/75) : 609 ex

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